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OPTICALLY DETECTED ADIABATIC INVERSION IN PHOSPHORESCENT TRIPLET STATES AND THE MEASUREMENT OF INTRAMOLECULAR ENERGY TRANSFER PROCESSES

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Optically Detected Adiabatic Inversion in Phosphorescent Triplet States

and the Measurement of Intramolecular Energy Transfer Processes

by

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Abstract

The theory and observation of microwave induced population inversion within triplet magnetic sublevels in zero field are presented. It is shown that inversion via adiabatic fast passage can be measured quantitatively by changes in triplet phosphorescence and that population inversion can be accomplished easily and with microwave field strengths even lower than are required for cw-saturation. Parameters affecting the ability to invert the sublevel populations such as dipolar interactions, microwave power and sweep rates are studied. General equations relating the intensity of phosphorescence and the fraction of inversion to

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parameters associated with energy transfer processes into and from the triplet state such as intersystem crossing, radiative and radiationless relaxation are derived and measured for the $^3\pi\pi^*$ state of 2,3-dichloro-quinoxaline.

I. Introduction

Optically detected magnetic resonance (ODMR) in zero field provides a power technique for investigating many different properties of aromatic and azaaromatic molecules in their triplet states.[1] A few parameters associated with electron distributions in excited triplet states such as the zero-field splitting of the magnetic sublevels, the nuclear-electron hyperfine and nuclear quadrupole coupling constants can be determined from an analysis of the fine structure in the EPR transitions. In addition, techniques have evolved to determine other properties of the triplet state such as the routes and rates of intramolecular energy transfer.[2,3,4] Specifically, the intensity and polarization of phosphorescence can be modulated by connecting the magnetic sublevels of the triplet with a resonant microwave field. Analysis of these changes makes it possible to determine the relative rates of intersystem crossing into the individual magnetic sublevels in addition to the radiative and radiationless decay rates from the sublevels to the ground state vibrational manifold. Several techniques have been developed to accomplish these ends.

One, that described by Schmidt, Veeman and van der Waals[2] utilizes the difference in triplet state magnetic sublevel lifetimes to measure the microwave induced intensity changes in the phosphorescence decay. Another method, described by/El-Sayed[3] quantitatively measures the micro-wave induced phosphorescence under steady-state illuminating conditions.

Common to the above techniques are the assumptions that spin lattice relaxation between the magnetic sublevels is negligible and that satura-tion of the sublevels by the microwave field can both' a) be achieved,

and b) does not cause adverse effects such as heating or more subtle perturbations associated with strong rf fields. An additional assumption implied in the steady state approximation is that the populations of the excited singlet states are independent of any microwave perturbation.

A third method has been outlined[4] for the measurement of the relative rates of intersystem crossing; however, the details have not heretofore been presented. This method relies on the fact that inversion of the magnetic sublevel populations by adiabatic fast passage can be accomplished with low microwave power and, more importantly, the fraction of inversion can be qualitatively measured. The virtue of this technique is that the population inversion can be applied under a variety of experimental conditions. Indeed, it can be used to eliminate the assumption of complete saturation in the decay techniques and steady state methods and in this way it can be applied to the measurement of all the salient rate constants.

In the following sections of this paper the theory and observations of adiabatic inversion of the triplet magnetic sublevel populations in zero field will be presented. Next, the application of adiabatic inversion to the determination of all the rate processes associated with a phosphorescent triplet state will be developed and applied to the triplet $\pi\pi^*$ state of 2,3-dichloroquinoxaline doped in tetrachlorobenzen. Finally, the different techniques will be compared.

II. Optically Detected Adiabatic Inversion in Zero Field

In order to simplify the discussion of adiabatic inversion for a molecular triplet state in zero field in the presence of a linear polarized microwave field connecting two of the three magnetic sublevels we will consider the problem in the framework of the interaction representation. The interaction representation can be viewed as a unitary transformation of the laboratory frame which removes the zero-field Hamiltonian. The effective Hamiltonian in the rotating frame is non-secular unless the applied microwave field is resonant in which case the Hamiltonian becomes secular in first order and has the form of a Zeeman Hamiltonian in its rotating frame. Thus zero-field magnetic resonance of a triplet state can be viewed as that of an integral Zeeman spin system in the interaction representation.

The clarifying feature of this approach is that the motion of the magnetization in the interaction representation is equivalent to the dynamics of the zero-field alignment of the populations associated with the magnetic sublevels in the laboratory frame. It is well known that the magnetization of a Zeeman spin system can be inverted adiabatically by several methods. One, that using π pulses, requires H_1 fields that exceed the local dipolar field in order to insure that all spins are identically prepared in the time duration of the pulse. Another, adiabatic fast passage, follows directly from the adiabatic theorem which states that if the time variation of the effective field H_{eff} (in the present case $H_{eff} = \gamma H_1$) is slow enough, then the magnetization will follow the instantaneous effective field in the rotating frame.

The experimental detection of adiabatic inversion in phosphorescent triplet states by optical means, i.e., monitoring the phosphorescences as a function of the microwave field, is relatively straightforward when rate processes associated with the individual magnetic spin sublevels are explicitly considered. Considering the intensity of emission from the magnetic sublevels as proportional to the rate times the population of the sublevels, the emission intensity to a particular vibronic level, I_o, is

$$I_o = \sum_{i=x,y,z} K_i N_i^o , \qquad (1)$$

where individual magnetic sublevel radiative rate constants are K_i and the instantaneous populations are N_i^o. If a microwave field is adiabatically swept through an electron spin transition, say $\tau_x \to \tau_y$, a certain fraction f of the population is transferred from one spin sublevel to the other and vice versa, while a fraction (1-f) is unchanged. This means that the population in the sublevels τ_x and τ_y after inversion are

$$N_x = (1-f) N_x^o + f N_y^o \qquad (2)$$

$$N_y = (1-f) N_y^o + f N_x^o , \qquad (3)$$

while τ_z remains unchanged. Consequently the intensity of phosphorescence after inversion becomes

$$I_1 = K_x[(1-f)N_x^o + f N_y^o] + K_y[(1-f)N_y^o + f N_x^o] + K_z N_z^o . \quad (4)$$

If the microwave field is swepth through resonance a second time at a time τ after the first passage and if τ is short compared to radiative

and radiationless relaxation processes, the population can again be altered, i.e.,

$$N_x = [1-2f+2f^2]N_x^o + [2f(1-f)]N_y^o \qquad (5)$$

$$N_y = [1-2f+2f^2]N_y^o + [2f(1-f)]N_x^o \quad , \qquad (6)$$

and the phosphorescence intensity again changes to a value I_2 where

$$I_2 = K_x[(1-2f+2f^2)N_x^o + 2f(1-f)N_y^o] + K_y[(1-2f+2f^2)N_y^o$$
$$+ 2f(1-f)N_x^o] + K_z N_z^o \quad . \qquad (7)$$

Using Eq.(2-7) it is obvious that f, the fraction of inversion, is simply related to the measured phosphorescent intensities and is independent of both polarization effects and the populations associated with the τ_z sublevel. Thus the above equations yield

$$f = 1 - \frac{1}{2}\left[\frac{I_2 - I_o}{I_1 - I_o}\right] . \qquad (8)$$

It should be noted that in the event saturation is achieved via the first fast passage then $f = \frac{1}{2}$ and the phosphorescence intensity is unchanged by the second inversion, that is $I_1 = I_2$.

The above sequence is illustrated diagrammatically in Fig. la and experimentally for 2,3-dichloroquinoxaline in Fig. lb. The details of Fig. lb are given in the experimental section. Figure lb illustrates an obtainable f factor for adiabatic inversion via fast passage of 0.86. The lack of a 100% inversion is probably in large measure due to the consequences of forbidden simultaneous nuclear-electron transitions.

It is known[5] that the zero-field transitions of 2,3-dichloroquinoxaline consists of a manifold of states split by the N^{14} nuclear hyperfine and N^{14} nuclear quadrupole interactions. In the present case in addition to sweeping through the allowed transition we were forced, because of resolution difficulties, to sweep through several simultaneous N^{14} and electron spin transitions which have low ($\sim 10^{-1}$) transition moments. Consequently, the f factor is reduced from what it would be in the absence of these forbidden transitions. In all likelihood the electron-only transitions would have f's close to unity.

III. Determination of Triplet State Parameters from Adiabatic Inversion Experiments

1. General Equations

The determination of the relative populations and intersystem crossing ratios of two triplet sublevels follows directly from Eqs.(1-8). Since the fraction of inversion, f, is determined via Eq.(8) from a measurement of I_0, I_1, and I_2, one must determine population ratios using only I_0 and I_1 or I_0 and I_2, to avoid mathematical redundancy. Having determined f by Eq.(8), the ratio of Eqs.(4) and (1) yields for population inversion of the x and y sublevels

$$\lambda^{xy} \equiv \frac{I_1^{x,y}}{I_0^{x,y}} = \frac{K_x[(1-f)N_x^O + f\,N_y^O] + K_y[(1-f)N_y^O + f\,N_x^O] + K_z N_z^O}{K_x N_x^O + K_y N_y^O + K_z N_z^O} \tag{9}$$

where the superscripts indicate which two levels were inverted. There are three such equations, one for each of the three zero-field transitions. Equation (9) contains six unknowns in addition to f; these are N_x^O, N_y^O, N_z^O, K_x, K_y and K_z. Therefore, for the most general case in which all three sublevels emit to the vibronic level being monitored, information from inversion experiments alone is insufficient to determine all parameters. However, the ratios $K_i N_i^O / K_j N_j^O$ are obtainable from a decomposition of the phosphorescence decay curve. These ratios combined with Eq.(9) are sufficient to determine the relative triplet sublevel populations. For many triplet states not all of the magnetic sublevels are active to all vibronic bands. In such cases the equations become simplified. For a case where only one of the levels, say τ_y, emits, Eq.(9) reduces to

$$\lambda^{xy} = \frac{K_y[(1-f)N_y^O + f\ N_x^O]}{K_y N_y^O} \tag{10}$$

Therefore,

$$\frac{N_x^O}{N_y^O} = \frac{\lambda^{xy} + f - 1}{f} \quad , \tag{11}$$

and the population ratios are obtainable solely from adiabatic inversion measurements. In another special case where τ_x and τ_y emit to the monitored optical band, it is easily shown by defining ϵ as

$$\epsilon = \frac{I_2^{x,y}}{I_1^{x,y}} \quad , \tag{12}$$

that

$$\frac{N_x^o}{N_y^o} = \alpha = \left[\frac{\epsilon+1-2f-2(1-f)\lambda}{1-2f+\epsilon\lambda-2(1-f)\lambda}\right]^{\frac{1}{2}}, \qquad (13)$$

and

$$\frac{K_y}{K_x} = \frac{(1-f-\lambda)\alpha+f}{\lambda+f(1-\alpha)-1}. \qquad (14)$$

Thus adiabatic inversion data yield both population ratios and the radiative rate constant ratios for the two levels connected by the microwave field. The number of possible combinations of rate constants are too numerous to analyze individually; however, the method outlined above can be modified to accommodate other cases.

The above technique assumed that the time between inversions, τ, was small compared with the triplet state deactivation rates. It is not necessary to limit τ in such a manner (except to determine f accurately). General equations can be written to consider explicitly the decay processes which result from disturbing the steady state. This approach expresses the population of level i as a function of time and is given in the following equations:

$$N_i(t) = [N_i^o - N_i^e] e^{-k_i t} + N_i^e, \qquad (15)$$

where N_i^o is the population at $t = 0$, N_i^e is the equilibrium population at $t = \infty$ ($N_i^e = 0$ if no exciting light is present and $N_i^e = N_i^{ss}$, the steady state equilibrium population if exciting light is present) and k_i is the total decay rate of level i. For example, if $N_i^e = N_i^{ss}$ (i.e., the

exciting light is left on), then for a case where $K_y \gg K_x, K_z$, and inverting levels τ_x and τ_y,

$$\lambda^{x,y}(t) = \frac{K_y \left[\left\{ [(1-f)N_y^{ss} + fN_x^{ss}] - N_y^{ss} \right\} e^{-k_y t} + N_y^{ss} \right]}{K_y N_y^{ss}} \qquad (16)$$

$$= 1 + f \left[\frac{N_x^{ss}}{N_y^{ss}} - 1 \right] e^{-k_y t} \qquad (17)$$

when inversion is performed at $t = 0$. Equation (17) reduces to Eq.(11) for $t = 0$. Equation (17) can be expressed in terms of logarithms as

$$\ln \left[\frac{\lambda(t)-1}{1} \right] = \ln \left[\frac{N_x^{ss}}{N_y^{ss}} - 1 \right] - k_y t \quad . \qquad (18)$$

A plot of Eq.(18) gives the values k_y and N_x^{ss}/N_y^{ss} more accurately in certain cases since one obtains many points as a function of t. Values for the steady state population ratios combined with triplet sublevel decay rates yeild intersystem crossing ratios since

$$\frac{N_y^{ss}}{N_x^{ss}} = \frac{k_y^I}{k_x^I} \cdot \frac{k_x}{k_y} \qquad (19)$$

where the k_i^I are the appropriate intersystem crossing rate constants.

The adiabatic inversion technique is complementary to the conventional ESR method developed by Schwoerer and Sixl.[6] The ODMR technique enables a direct quantitative determination of the population and intersystem crossing rate ratios to be made while the complex nature

of the equations involved in the conventional ESR method make quantitative measurements difficult.

A general requirement of the adiabatic inversion technique is that there be a reasonable population difference between the two levels being inverted since the change in the optical signal is proportional to $N_i - N_j$. This technique is applicable in any case where cw-saturation experiments[3] are useful and should be more sensitive. In the next section we apply the adiabatic fast passage population inversion technique to 2,3-dichloroquinoxaline in a tetrachlorobenzene host.

2.   Application to 2,3-Dichloroquinoxaline

The optical and microwave spectra of 2,3-dichloroquinoxaline doped in durene have been analyzed by El-Sayed et al.[3,7] and Harris et al.[5] respectively. The corresponding spectra in a tetrachlorobenzene host are only slightly different. The zero-field level orderings and splittings are shown in Fig. 2. Phosphorescence decay curves were obtained by monitoring either the origin (4679 Å) or the band at 4739 Å $(0,0-260 \text{ cm}^{-1})$. Both bands decayed as single exponentials with decay rates of 5.77 sec^{-1} and 7.13 sec^{-1} respectively. This is consistent with the results in a durene host:[3] The 0,0 band originates from τ_z and the 0,0-260 cm^{-1} band originates from τ_y. A small amount of emission ($\sim 5\%$) was present in the origin which decayed with a lifetime of ~ 2 sec, which undoubtedly originates from τ_x, and again is consistent with the decay scheme[3] in a durene host. The similarity of dichloro-quinoxaline in the two hosts is further supported by PMDR results in

which a change in intensity of the origin is observed in the 1.05 GHz or 3.5 GHz transition but not for the 2.5 GHz transition. Likewise, the 0,0-260 cm^{-1} band is coupled only to the 2.5 GHz and 1.05 GHz EPR transitions. Thus, dichloroquinoxaline in tetrachlorobenzene is an easy test case for adiabatic inversion measurements since the simplified Eq.(11) can be used insofar as one sublevel, to a good approximation, emits to each of the two abovementioned bands. Previous experiments[3] have shown that $N_x \approx N_y \approx 6N_z$ in a durene host. Since the relative triplet sublevel lifetimes are changed only slightly on going to a tetrachlorobenzene host, the same relative sublevel populations are expected as are found in a durene host. Inversion of the 1.05 GHz transition should increase the intensity of the origin and decrease the intensity of the 0,0-260 cm^{-1} band by a factor of ~ 6. The observed changes given in Table I as I_1/I_0 are about a factor of 7; thus, the population ratios obtained via adiabatic fast passage measurements are indeed close to those previously determined[3] by steady state methods. Using Eq.(8), the fraction of inversion obtained in Fig. 1b was 0.86. (Use of a better matched slow-wave helix yielded inversion fractions as high as 0.93.) The data obtained from identical inversion experiments utilizing the equations developed in Section II and all three zero-field transitions while monitoring the origin and 0,0-260 cm^{-1} band are summarized in Table I. From the measured decay rates of τ_x and τ_y (5.77 and 7.13 sec^{-1} respectively) and the value of $N_y/N_z = 8.00$, one obtains $k_y^I/k_x^I = 9.0$. This is lower than the value of ~ 15 reported by Tinti and El-Sayed[3] for the durene host. This reduction may be due to the external

heavy atom effect of the tetrachlorobenzene host. The above decay rates
and intersystem crossing rates were used to calculate the predicted
change in intensity of the origin upon saturation of the 1.05 GHz
transition using Eq. 12d of Ref. 3. The intensity change was measured
and found to be approximately 10% smaller than that predicted. This is
consistent with the lack of complete saturation obtainable in this
system (See Section IV).

Examination of Table I shows apparently inconsistent values for the
N_y/N_z ratios obtained monitoring two different optical bands. The value
obtained monitoring the 0,0-260 cm^{-1} band is inaccurate because the
solution of Eq.(11) accidentally gives in the numerator a small difference
of two large numbers. Such unfortunate arithmetic did not occur in the
evaluation of other ratios. Specifically, the experimentally determined
N_y/N_x ratio obtained monitoring the 0,0-260 cm^{-1} band is close to that
calculated from data obtained monitoring the origin. The ratios obtained
by monitoring the origin were used in calculating the intersystem cross-
ing ratios given above.

IV. Comparison of Adiabatic Inversion and Saturation

The ease of obtaining inversion points out the importance of dipolar
quenching. This can be understood more completely from the conditions
imposed by the adiabatic theorem. For complete inversion of the magneti-
zation in rotating frame or population inversion in laboratory frame
in a system of free spins,
the relationship between the applied field H_o in the presence of a radio-
frequency field of frequency ω and magnitude H_1 and local dipolar fields

$\Delta H_{\ell oc}$ is

$$\frac{dH_T}{dt} = \frac{dH_o}{dt} < \gamma H_1^2 \qquad (20)$$

$$H_1 > \Delta H_{\ell oc} \quad . \qquad (21)$$

Equation (20) is the adiabatic theorem and insures that the magnetization is always aligned along the instantaneous total field $H_T = H_o + H_1$. For a real spin system an additional requirement must be met. The adiabatic inversion must take place in a time short compared with any relaxation processes in the spin system. Thus if τ is the time required for passage through resonance, then[8]

$$\tau < H_1 \bigg/ \frac{dH_o}{dt} < T_2 < T_1 \, , \qquad (22)$$

where T_1 and T_2 are the characteristic longitudinal and transverse relaxation times of the system. In a coordinate frame rotating about an applied field H_o at a frequency ω,

$$H_T = H_o + \frac{\omega}{\gamma} \qquad (23)$$

$$\frac{dH_T}{dt} = \frac{dH_o}{dt} + \frac{1}{\gamma} \frac{d\omega}{dt} \, . \qquad (24)$$

In _zero_ field, $\frac{dH_T}{dt} = \frac{1}{\gamma} \frac{d\omega}{dt}$; thus, adiabatic inversion can be accomplished by changing ω, the frequency of the applied RF field.

As was mentioned above, large fractions of inversion (> 80 percent) are relatively easy to obtain.[9] In an effort to determine the bounds

of some of the quantities expressed in Eqs.(20-22), a study of the

inversion factor as a function of H_1 and dH_1/dt was made. A plot of

f vs. dH_1/dt (or rather $d\omega/dt$) is shown in Fig. 3. For these measure-

ments the origin of the 2,3-dichloroquinoxaline phosphorescence was

monitored while sweeping the applied microwave frequency through the

1.05 GHz resonance at various rates (0.1 to 40 milliseconds per 16 MHz),

and using Eq.(8) to determine f. One watt of rf power was used;

however, the actual power delivered to the sample was probably closer

to 0.01 w. which corresponds to a field strength of approximately 0.1

gauss at the sample.[10] The important feature of Fig. 3 is that adiabatic

inversion can be accomplished with very long sweep times. A rough

estimate of T_2 can be made utilizing Eq.(22), i.e.,

$$\frac{T_2}{\Delta t} > \frac{2 \gamma H_1}{\Delta \nu} \quad , \tag{25}$$

where a frequency $\Delta \nu$ was swept through in a time Δt. For $H_1 \sim 0.1$ gauss

and $\Delta t = 40$ ms, $T_2 > 10^{-2}$ sec. This result is at first sight surprising

since the EPR linewidths are ~1 MHz, which implies $T_2 \sim 10^{-6}$ sec.

However, the T_2 in Eq.(22) is the homogeneous T_2, while the linewidth

is a sum of both a homogeneous T_2 and an inhomogeneous T_2^*, i.e.,

$\Delta \omega = \frac{1}{T_2} + \frac{1}{T_2^*}$. This result is qualitatively consistent with quenching

of dipolar coupling for integer spin systems in zero field. The quench-

ing can be removed by the application of an external magnetic field.[11]

A study of the fraction of inversion as a function of an external mag-

netic field showed that f was reduced as anticipated from 0.93 in zero

field to 0.5 in a 200 gauss field. To obtain another measure of T_2,

one can estimate ΔH_{loc} via the condition implied by Eq.(21). Figure 4b

shows a plot of f vs. applied microwave power. Full power (0 dB)

represents an rf field (H_1) of approximately 0.05 gauss. At approximately

10 dB attenuation ($H_1 = 5\times10^{-3}$ gauss) the inversion factor has been re-

duced to 0.5 (i.e., saturation). This implies local fields less than

$\sim 5\times10^{-3}$ gauss, or a T_2 longer than $\sim 10^{-4}$ sec. This is in qualitative

agreement with the aforementioned resulted for the dH/dt study.

The decay methods[2] and steady state methods[3] depend upon the ability

to attain complete saturation of zero-field spin sublevels in order to

quantitatively interpret the experimental results. Generally saturation

is easily attainable in zero field at low temperatures, particularly if

a high Q microwave cavity is used. However, depending upon the sample,

the available microwave power and the cavity, saturation may not be

possible. This is particularly true of low Q broad-banded slow wave

helical cavities. Such a case is illustrated in Fig. 4a which shows

the phosphorescence intensity (origin) of 2,3-dichloroquinoxaline as a

function of power while saturating the 1.05 GHz zero-field transition.

The lack of a plateau at high power clearly indicates incomplete satura-

tion. The same saturation curves were obtained when the microwave field

was modulated over the entire linewidth implying the lack of saturation

is not due to the lack of spin diffusion. Figure 4b shows the fraction

of inversion for the same transition using the same power and sample.

It is apparent that inversion fractions greater than 0.5 are attainable

via adiabatic fast passage at power levels at least a hundred times

smaller than required for saturation via application of continuous

microwave power; thus, the relative ease of adiabatic inversion may make it a preferred technique in some cases. An additional limitation of saturation techniques which require high continuous power is lack of temperature control due to heat dissipated in the sample. Since power need only be applied to the sample during passage through resonance in an adiabatic inversion experiment (see Section V), the rms power dissipated in the sample can be reduced by many orders of magnitude. A further difficulty can arise in the application of saturation methods to molecules with very short lifetimes due to the inability to saturate within a lifetime. Adiabatic inversion techniques may prove to be a better method in such cases. A general advantage of the inversion method is that populations can be sampled in a very short time -- e.g., microseconds. Another (usually) very small source of error in saturation experiments is the microwave effect on the singlet and ground state populations at saturation. Because adiabatic fast passage experiments can be accomplished on a time scale much shorter than triplet state decay times, any change in relative triplet sublevel populations cannot be communicated to the ground state and thus to the excited singlet state by reabsorption.[12]

In summary, saturation experiments are a useful and powerful technique in the library of optically detected magnetic resonance methods; however, in certain specific cases caution is necessary. Adiabatic inversion provides a complementary technique useful in eliminating many of the potential sources of error in saturation and decay methods.

V. Experimental

Samples of 1,2,4,5-tetrachlorobenzene and 2,3-dichloroquinoxaline were purified by repeated zone refining (200 passes at 2 hours per pass) and recrystallization followed by vacuum sublimation, respectively. A single crystal sample of 2,3-dichloroquinoxaline in tetrachlorobenzene ($\sim 10^{-3}$ m/m) was grown by standard Bridgeman technique. Microwave power was obtained from a Hewlett-Packard Model 8690-B sweep oscillator used in conjunction with a Servo Corp. Model 2220 Microwave power amplifier. AM and FM modulation signals for the sweep oscillator were obtained from a General Radio type 1395-A pulse generator. Microwave power was applied to the sample through a rigid coaxial line terminated with a slow wave helix. The sample was suspended in a liquid helium dewar with the sample in contact with liquid helium. Temperatures below 4.2°K were obtained by pumping on the liquid helium. Phosphorescence was detected through a Jarrell-Ash 3/4 M Czerney-Turner spectrograph. Light from a PEK-100 watt mercury arc lamp was focused through a water filter and a Schott 3100 Å interference filter for excitation. A block diagram of the experimental setup is shown in Fig. 5. All measurements were made at 1.35°K.

The frequency sweep required to invert the triplet sublevels was obtained by applying a ramp voltage to the F.M. input of the microwave sweep generator. The ramp voltage (V) was adjusted so that when $V = V_0$, the microwave frequency was ω_0, the center of the EPR transition being used for inversion (see Table I and Fig. 6). The F.M.

voltage was swept linearly from $V_o - \frac{1}{2}v$ to $V_o + \frac{1}{2}v$ in a time τ so that the microwave frequency change from $\omega_o - \frac{1}{2}\delta$ to $\omega_o + \frac{1}{2}\delta$ (see Table I) in a time τ. After a time Δ, the frequency was swept back from $\omega_o + \frac{1}{2}\delta$ to $\omega_o - \frac{1}{2}\delta$. Thus by varying τ and fixing δ one varies dH/dt (Eq. (24)). The data in Fig. 3 were obtained by varying τ from 0.1 to 40 milliseconds. To obtain the best signal-to-noise ratio the inversion was performed at 4-second intervals (to allow reestablishment of steady-state conditions), each inversion signal being fed into a PAR Waveform Eductor. This averaging technique greatly improved signal-to-noise ratios over simply photographing one sample displayed on an oscilloscope. This method was used for the inversion measurements (Fig. 3,4) saturation measurements shown in Fig. 4, and phosphorescence lifetime measurements. To minimize any heating effects, microwave power was applied to the sample only during passage through resonance. Microwave power was applied by using an offset squarewave pulse to the A.M. input of the microwave sweeper.

The time between inversion, Δ (see Fig. 6), was zero for the 10, 20 and 40 ms points in Fig. 3 and 0.5 ms for all other data. The values of δ for the three zero-field transitions are listed in Table I. The microwave sweeper could follow F.M. Signals which produced a change of 10 MHz in 80 μsec. Thus to insure linearity in the frequency sweep, τ values below 100 μsec were not used. Since the total time for determining f values $(2\tau + \Delta$; Fig. 6) was 0.7 ms and the phosphorescence lifetimes of the 2,3-dichloroquinoxaline are ~100 ms, errors introduced

by triplet decay and intersystem crossing were negligible in the determination of the triplet sublevel populations and intersystem crossing rates (Table I).

The power level changes for the data in Fig. 4 were made by inserting Hewlett-Packard precision microwave power attenuators in the transmission line.

VI. Acknowledgments

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9. The conditions for fast passage in solids are determined in large measure by the local fields seen by the spin system. The presence of a dipolar spin system different from that associated with the resonant spin produces a local field, $\Delta H_{\ell oc}$, which, through magnetic dipole-dipole interactions, essentially adds to the effective field H_{eff}. If these local fields vary then the magnetization will follow the resultant field $H_{eff} + H_{\ell oc}$; so unless the local fields are much smaller than the effective field and unless adiabatic inversion of the magnetization occurs faster than the relaxation time, adiabatic inversion will be incomplete. Ordinarily, adiabatic inversion is at best difficult in solids in high magnetic fields. A triplet state in zero field would not, however, by subject to the same restrictions as a spin system in high fields. The local dipolar field as seen by the triplet states is expected to vanish in first order in the absence of an applied magnetic field. As a result, the contribution of the dipole-dipole terms to the linewidths vanishes and adiabatic inversion of the magnetization in the rotating frame or, equivalently, population inversion of the magnetic sublevels in the zero-field laboratory frame may be expected to occur at reasonably low H_1 fields. The reduction of the local field as seen by the triplet spin system -- dipolar quenching -- can be understood by analogy

with the well-known quenching of integral nuclear spins in zero field[11] or the quenching of integral orbital angular momentum of electronic states (J. H. van Vleck, Phys. Rev. $\underline{74}$, 1168 (1948)). Specifically, in the interaction representation the dipolar Hamiltonian contains only non-secular terms when no generacy associated with the spin eigenstates exists (J. Schwab and E. L. Hahn, J. Chem. Phys. $\underline{52}$, 3152 (1970)). Consequently, in first order the coupling of the local dipolar field to the integral spin system vanishes in zero field. Applied to a triplet state in zero field, this means that when the molecule possesses an asymmetry around the principal zero-field tensor axis (i.e., the triplet state has a finite E value) it may not be unreasonable to expect adiabatic inversion of the magnetic sublevel populations to occur at $\underline{lower}$ H_1 fields than are necessary for saturation. Indeed such has been observed in the phosphorescent triplet $\pi\pi^*$ state of 2,3-dichloroquinoxaline and other $n\pi^*$ and $\pi\pi^*$ aromatic triplet states (M. J. Buckley, C. B. Harris and R. M. Panos, unpublished results).

10. Microwave field strength measurements are obtainable from inversion experiments using π-pulses.[4] Experiments similar to those reported by Schmidt $\underline{et}$ $\underline{al}$. (J. Schmidt, V. C. van Dorp, and J. H. van der Waals, Chem. Phys. Letters $\underline{8}$, 345 (1971)) were performed and a measure of H_1 obtained (See Eq. 12 of Ref 4 and Eq. 11 of Schmidt $\underline{et}$ $\underline{al}$.).

11. G. W. Leppelmeier and E. L. Hahn, Phys. Rev. $\underline{141}$, 724 (1966).

12. If one considers an aromatic molecule with a lowest excited singlet state lifetime of $\sim 10^{-8}$ sec and typical values of intersystem crossing rates and triplet state lifetimes with $k_x^I > k_y^I$ and $k_x > k_y$ so that $N_x/N_y \sim 10$ one finds (C. B. Harris and R. J. Hoover, unpublished results) from the steady state solutions of the differential equations describing the populations of the excited and ground states that saturation of the $\tau_x - \tau_y$ zero-field transition changes the total excited triplet state population by a factor of five and the lowest excited singlet state population by about five percent. The important point is that a change in fluorescence intensity of a per cent or so is easy to measure and thus the detection of zero-field ERS transitions by monitoring fluorescence is feasible. The quantitative interpretation of such a change in fluorescence can then be used to determine individual intersystem crossing rates directly.

Table I

Summary of Experimental Adiabatic Fast Passage Inversion Results

for 2,3-dichloroquinoxaline

0,0-Band

ω_o^a	f^b	I_1/I_o^c	δ^d	Power^e	N_y^o/N_z^o	N_y^o/N_x^o	N_x^o/N_z^o
1.05	0.88	7.15	16	1.2	8.00	-	-
2.45[h]	0	-	-	-	-	3.47[f]	-
3.50	0.85	2.20	30	1.0	-	-	2.30

0,0-260 cm^{-1} Band

ω_o^a	f^b	I_1/I_o^c	δ^d	Power^e	N_y^o/N_z^o	N_y^o/N_x^o	N_x^o/N_z^o
1.05	0.90	0.166	16	1.2	13.5[g]	-	-
2.45	0.81	0.56	4	10.0	-	3.50	-
3.50[h]	0	-	-	-	-	-	3.8[f]

[a] Zero-field transition used for inversion, GHz.

[b] Fraction of inversion obtained.

[c] Ratio of phosphorescence intensities after and before inversion.

[d] Frequency range swept through to obtain inversion - a sweep time of 100 µsec was used (see experimental section), MHz.

[e] Applied power, watts: one watt gives an effective field of approximately 0.1 gauss.

[f] This value is obtained from the ratio of the two other ratios.

[g] This value is very uncertain because in applying Eq.11 the numerator results from the subtraction of two large numbers to yield a small number with a consequently high error.

[h] Excitation of this zero field transition produces no change in phosphorescence intensity.

Figure Captions

Figure 1.　(a) Schematic representation of the phosphorescence intensity change produced by inverting the populations of two magnetic triplet sublevels. The phosphorescence originates from the level having the smaller steady state population in the illustration. The intensity increases to the value at (1) upon inversion. After a short time the populations are inverted again and the phosphorescence intensity changes to the value at (2). The value at (2) is larger than the initial steady-state value because the fraction of inversion (see text) is less than unity. The dashed line shows decay due to radiative and non-radiative processes.

(b) Oscilloscope tracing of the phosphorescence origin of 2,3-dichloroquinoxaline in a tetrachlorobenzene host while inverting the populations of the τ_y and τ_z sublevels by sweeping through the 1.05 GHz ESR transitions. The time between inversions was 10 ms; a fraction of inversion of 0.86 was obtained. One hundred milliwatts of microwave power was used, of which 100 µwatts probably reached the sample.

Figure 2.　Energy level diagram of the lowest triplet state of 2,3-dichloroquinoxaline. Heavy arrows indicate the principal phosphorescence routes.

Figure 3. Plot of the fraction of inversion in 2,3-dichloroquinoxaline

as a function of the time (τ) required to sweep through

resonance. The fraction of inversion is highest for short

sweep time (i.e., large dH/dt) because the "forbidden" electron-

nuclear transitions cannot follow the changing field and hence

cannot reduce the fraction of inversion as explained in the

text. Resonance was swept through in 100 microseconds.

Figure 4. (a) Phosphorescence intensity of 2,3-dichloroquinoxaline as

a function of applied microwave power. The non-uniform shape

of the curve is probably due to the power-dependence of the

mode pattern inside the helical slow-wave cavity.

(b) Plot of the fraction of inversion vs. applied microwave

power. Resonance was swept through in 100 microseconds.

Figure 5. Block diagram of the experimental arrangement.

Figure 6. Time dependence of microwave frequency (ω) and power (P)

(see text for details).
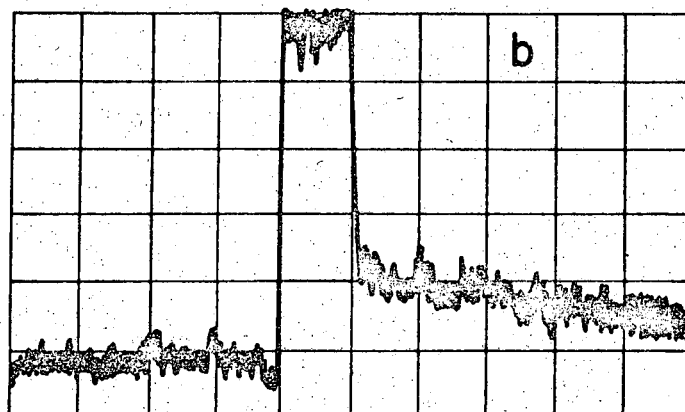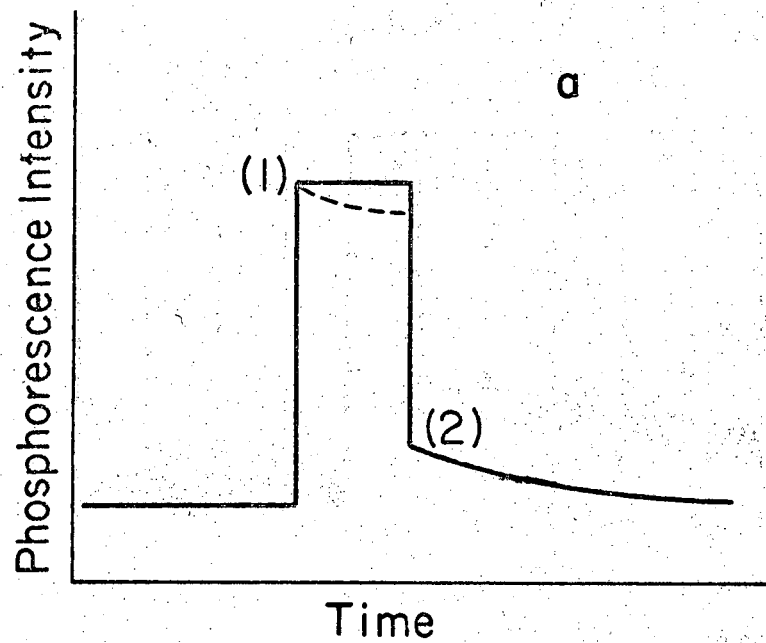
XBL 717-6926

Fig. 1
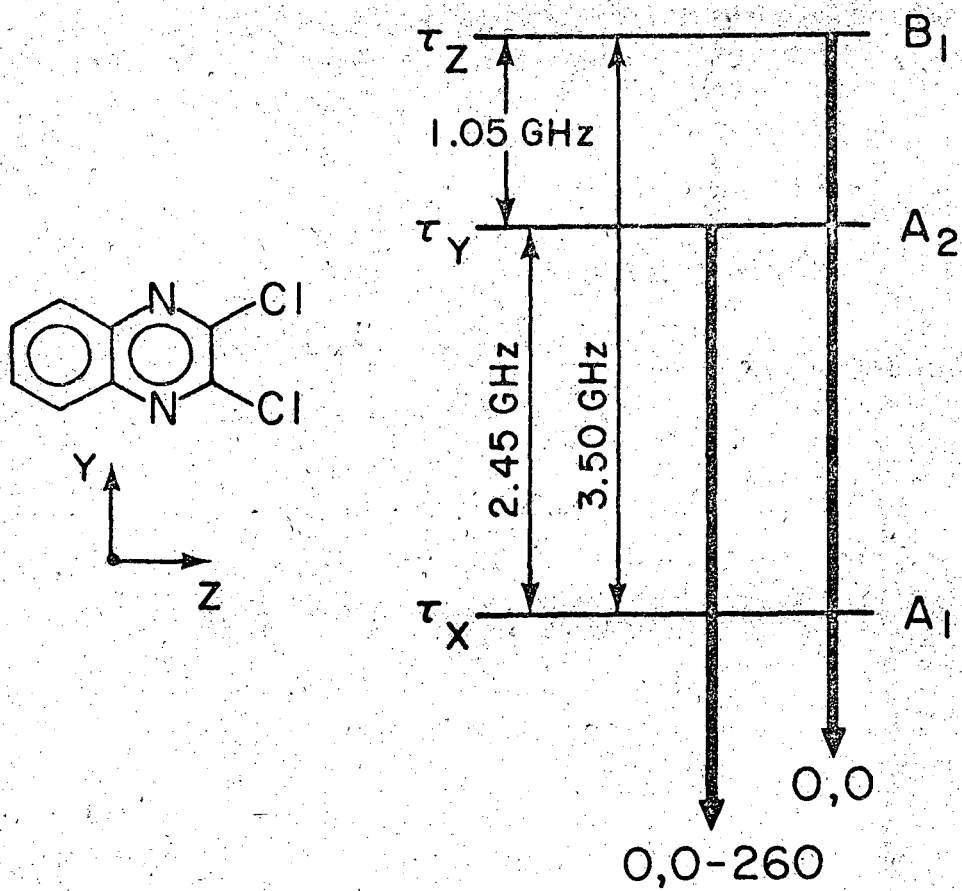
Fig. 2

XBL 716-6893
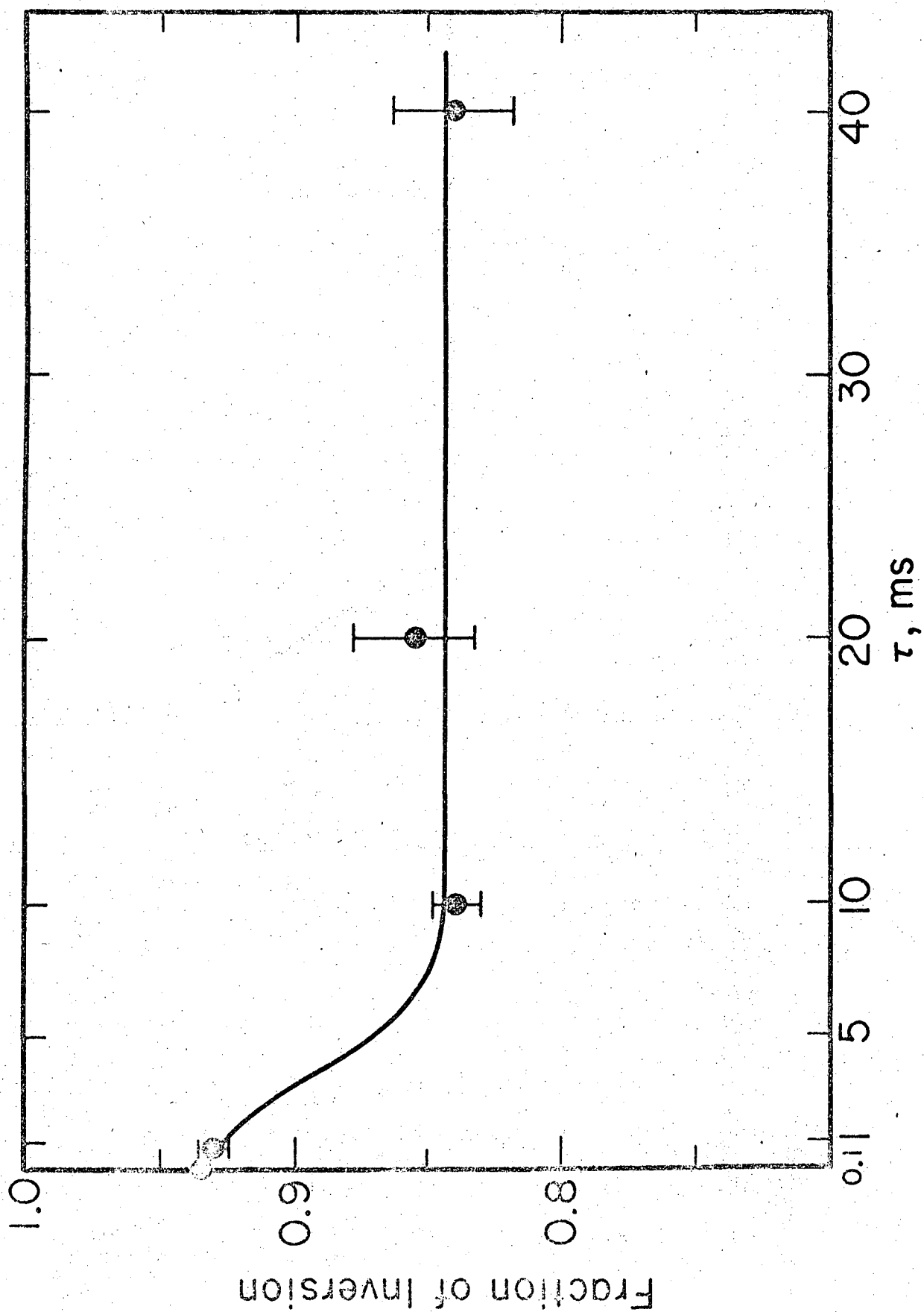
Fig. 3
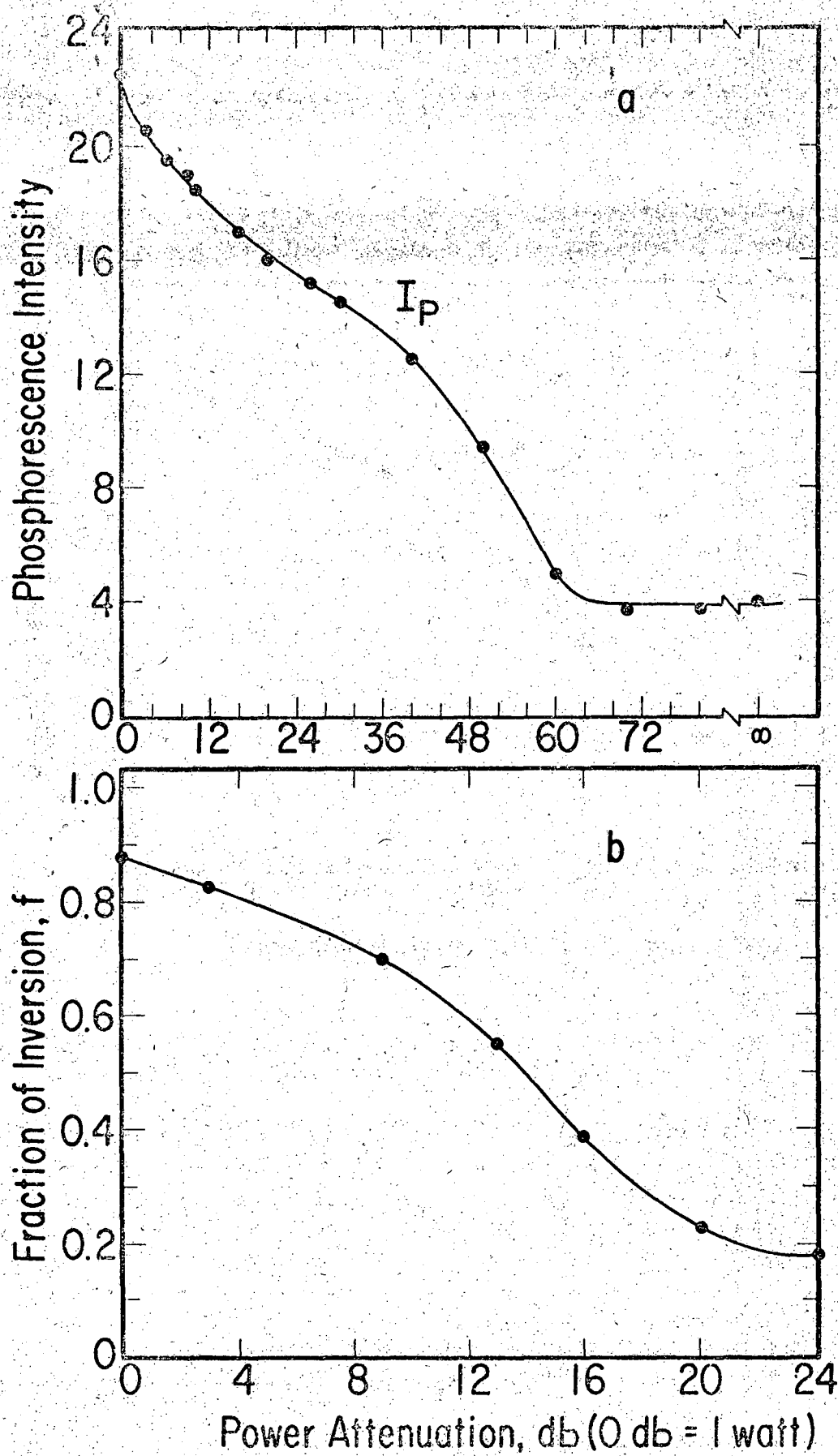
XBL 716-6896

Fig. 4

XBL 717-6925
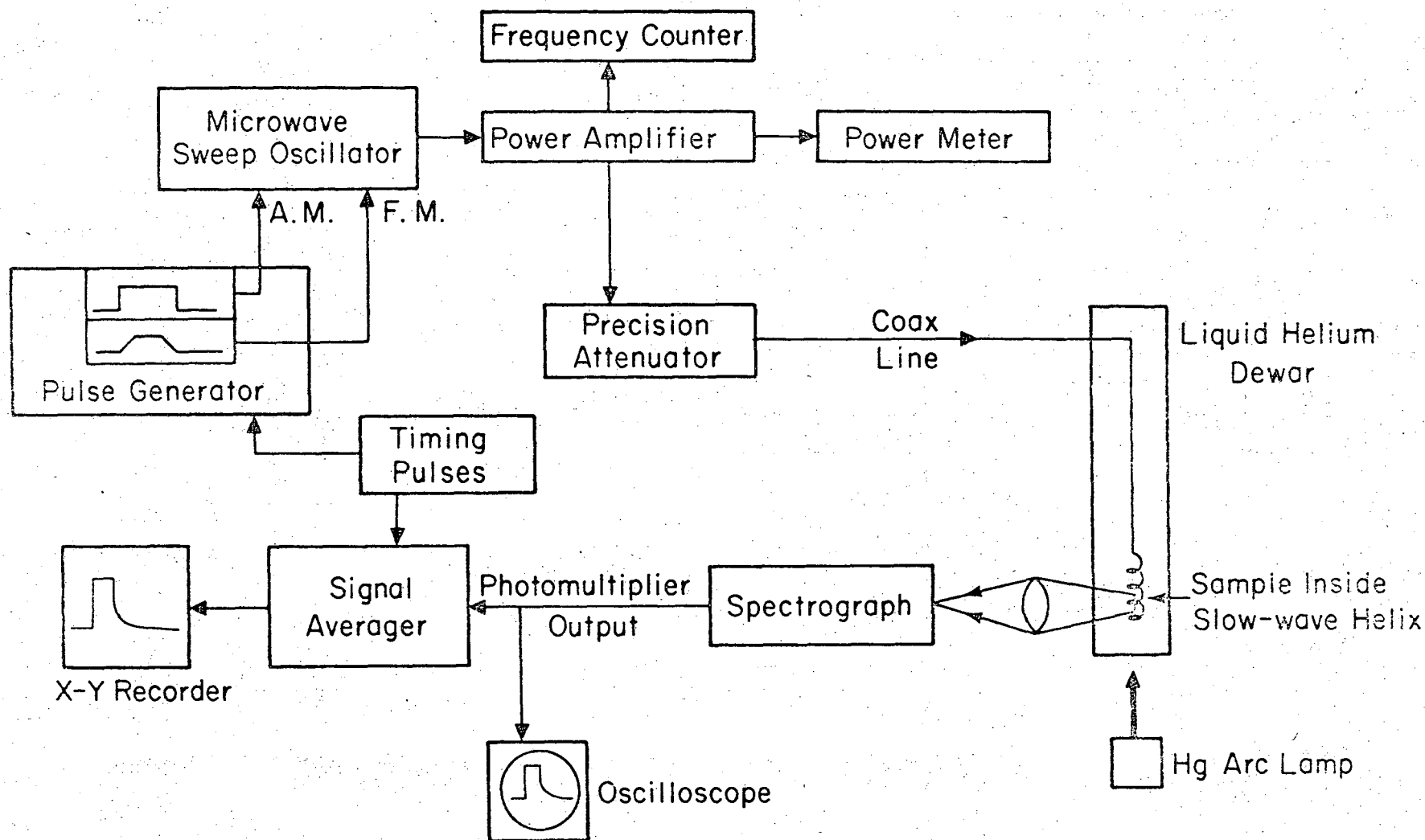
INSTRUMENTAL ARRANGEMENT

Fig. 5

Fig. 6

XBL 716-6895