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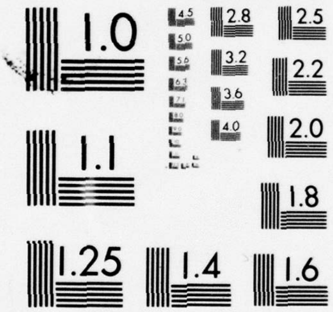
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# Optical Detection of Spectral Diffusion of the Triplet State Zerofield Transition Energy.

10 William M./Pitts ~~and~~ M. A./El-Sayed

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University of California
Department of Chemistry
Los Angeles, California 90024

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Pulsed EEDOR experiments using optical detection have been developed and utilized to study spectral diffusion within the inhomogeneously broadened zerofield spin transition of a photoexcited triplet molecule. Two distinct spectral diffusion processes have been observed. One is very fast and is the source of the rapid loss of spin coherence previously observed in spin echo experiments of photoexcited triplet molecules. This rapid spectral diffusion seems to be limited to a narrow range of frequencies within the inhomogeneous profile of the spin

(continued)

transition. The second phase is considerably slower, but can sample a greater range of frequencies within the inhomogeneous profile. This second spin diffusion process determines the minimum hole width which can be observed in a steady state EEDOR experiment.

# Optical Detection of Spectral Diffusion of the Triplet State Zerofield Transition Energy

William M. Pitts[†] and M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, California 90024

## Abstract

Pulsed EEDOR experiments using optical detection have been developed and utilized to study spectral diffusion within the inhomogeneously broadened zerofield spin transition of a photoexcited triplet molecule. Two distinct spectral diffusion processes have been observed. One is very fast and is the source of the rapid loss of spin coherence previously observed in spin echo experiments of photoexcited triplet molecules. This rapid spectral diffusion seems to be limited to a narrow range of frequencies within the inhomogeneous profile of the spin transition. The second phase is considerably slower, but can sample a greater range of frequencies within the inhomogeneous profile. This second spin diffusion process determines the minimum hole width which can be observed in a steady state EEDOR experiment.

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[†] Present address: Naval Research Laboratories, Chemistry Division, Code 6110, Washington, D.C. 20375.

## 1. Introduction and Objectives

In the recent past there has been a great deal of experimental work performed in order to determine the true homogeneous lineshapes of spectroscopic transitions which are masked by inhomogeneous broadening. Such experiments are important because the homogeneous lineshape reveals much about the nature of the quantum system undergoing the transition as well as the interaction of the system with its surroundings.

Two distinct experimental methods -- the Hahn echo(1) and spectral holeburning(2) - have been widely used to overcome the limitations of inhomogeneous broadening and to allow a study of underlying homogeneous spectral profiles.

Such studies have been performed for magnetic resonance transitions between spin states as well as for electric dipole transitions between rotational, vibrational, and electronic states. In this work we are concerned with the optically detected magnetic resonance transitions between the spin levels of photoexcited triplet states.

Measurements in zero field of magnetic resonance transitions between spin levels of triplet states isolated in single crystals at liquid helium temperature have revealed linewidths which have an observed full width half maximum (FWHM) of a MHz or greater.(3,4) Two different methods of spin echo decay measurements -- classical detection of magnetization(5) and an optical method using a microwave probe pulse(6) -- have revealed that for such systems the echo disappears with decay times of 2-16 μsec.(5,7,8) Such decay times should correspond to homogeneous profiles with FWHM of approximately 20 kHz to 160 kHz. Clearly the magnetic resonance transitions are inhomogeneously broadened.

Initial holeburning experiments(9) in a photoexcited triplet state confirmed that the observed optically detected width of the zerofield transitions of triplet s-tetrachlorobenzene (TCB) in durene is inhomogeneously broadened. However, the holes had FWHM on the order of MHz while a later spin echo measurement on the same guest-host system (in a single crystal) predicted a hole FWHM of approximately 80 kHz.(8)

Many other observations of holeburning in magnetic resonance transitions of triplet states have been reported,(10-15) but until recently no attempts have been made to relate these burned holes to homogeneous lineshapes found in spin echo experiments. Nishi et al.(16) have reported spin echo measurements for the triplet of photosynthetic bacteria isolated in a glass which indicate that the homogeneous lineshape has a FWHM consistent with that measured previously in holeburning experiments.(12,13)

The rapid spin echo decay of photoexcited triplet states has been attributed to a horizontal energy transfer process known as spectral diffusion. This term is a general term which has come to designate any of a large number of processes which can transfer saturation or partial saturation from one homogeneous packet of an inhomogeneous band to another. In the case of triplet spin levels isolated at low concentrations in single crystals, such spectral diffusion is believed to arise from fluctuations of local magnetic fields at the site of the triplet.(4, 5, 7,8) These local fields result from the presence of magnetic nuclei on the triplet molecule itself and on surrounding host molecules. Local magnetic fields are modulated when the nuclei undergo energy relaxation or spin-spin interactions. An identical spectral diffusion mechanism was found to be important in the decay of spin echoes of organic free radicals and ions isolated in rigid glasses.(17)

The experiment which has been used in the past to study holeburning in the spin transitions of photoexcited triplet states is optical detection of electron-electron double resonance (EEDOR).(18) To our knowledge all past holeburning experiments involving triplet states have used continuous wave (c.w.) application of the single frequency (stationary) holeburning microwave field and have monitored its effect by sweeping a second microwave source of variable frequency (swept) across the band.

It occurred to us that under these experimental conditions spectral diffusion could result in the observation of a hole in the inhomogeneous profile which is much larger than that predicted by its homogeneous lineshape. Two experiments have been developed to test this hypothesis. The first will be called single frequency pulsed EEDOR. A short microwave pulse of frequency $\nu$ is used to burn a narrow hole in the inhomogeneous profile of a spin transition. A second pulse of microwaves at the same frequency is applied to the sample after a delay time t'. The response of the phosphorescence intensity arising from the triplet due to the second pulse will depend on whether or not the hole has filled in due to spectral diffusion, $T_1$ relaxation processes, and triplet repopulation with an unperturbed spin level distribution. By varying t', the recovery of the hole at $\nu$ is monitored as a function of time. This experiment is similar to one performed by Mims et al. for inorganic systems.(19)

A second experiment -- swept frequency pulsed EEDOR -- provides the same information as single frequency pulsed EEDOR but for a wide range of swept frequencies. As before, a single frequency microwave pulse burns a hole at $\nu$, but in this experiment the effect of the first pulse is monitored at a different frequency $\nu_i$ by pulsing a second microwave source. By varying $\nu_i$ and repeating the pulse sequence it is possible to map out the effect of the single frequency microwave pulse across the entire inhomogeneous band of the transition. The time development of spectral diffusion is monitored by varying the time, t, between the two microwave pulses.

## 2. The System Studied

TCB isolated in a single crystal of durene was chosen for the initial studies using pulsed EEDOR techniques. The triplet of TCB has been widely studied and its previously measured dynamic properties(20-22) indicated that it would be an excellent choice.

Table 1 lists the dynamic and static properties of TCB when isolated in a single crystal of durene. Note that the radiative spin level to the zero vibrational level of $S_0$ is $\tau_B$.[†] This level is underpopulated relative to $\tau_A$ and when microwaves induce a transition between these two levels a large increase in the phosphorescence intensity is expected.

The initial c.w. EEDOR study of holeburning in photoexcited triplet states(9) was performed on the system chosen for study here. This experiment indicated that spectral diffusion might be playing a role in the observed widths of the hole.

This system has also been the object of many coherence experiments by Harris and his coworkers. The spin echo decay time for TCB in durene was found to be 4 μsec.(8) Results were also given for an experiment using a Carr-Purcell Meiboom-Gill pulse train.(8) They found that when such a pulse train was used the echo decay time was greatly extended. The resulting decays were nonexponential, but the source of this behavior was not discussed. Spin locking experiments yielded decay times approaching the triplet lifetime.(23)

Adiabatic demagnetization in the rotating frame was used to demonstrate that spectral diffusion was slow in the system TCB-$d_2$ in durene-$d_{14}$.(24) Similar experiments utilized cross relaxation in the rotating frame to demonstrate the importance of surrounding nuclei in triplet spin state dephasing processes.(4)

## 3. Experimental

Single crystals of zone refined durene doped with recrystallized TCB were grown using the Bridgman method. Nominal molar concentrations of TCB were either .4% or .04%.

Experiments were performed with the samples immersed in liquid helium either at 4.2 K or pumped to 1.5 K. Excitation of the TCB was accomplished with the

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[†] N, A, and B refer to the axes directions in the molecule. A passes through the carbon atoms, B passes through the bonds, and N is normal to the plane.

3130 Å line of a 100 W mercury lamp. The 0,0 band of the phosphorescence (3778 Å) was isolated by a Jarrell-Ash one meter spectrometer equipped with an EMI 9502S photomultiplier (PM) for optical detection.

The sample was placed in a terminated copper slow wave microwave helix designed to match the 50 Ω impedance of the coaxial transmission line.(25) Samples were cut and aligned so that the durene crystal axis was oriented along the axial direction of the helix. Such a configuration insures that both TCB molecules in the durene crystal unit cell(26) are affected by the same magnetic field strength of the microwaves.

All studies were conducted on the 2E spin transition of TCB. Microwave frequencies were chosen to insure that only the purely electronic spin transition might occur. For this reason it was not necessary to consider the weak magnetic resonance transitions associated with the simultaneous change of an electronic spin state and a nuclear quadrupole state of the chlorines.(21)

Two types of pulsed EEDOR experiments were done. In one -- swept frequency pulsed EEDOR -- two separate microwave generators were used. In this case a 90° coaxial hybrid coupler acted as an adder to allow the two different microwave outputs to pass down the single coaxial transmission line to the helix. In the second type of experiment -- stationary frequency pulsed EEDOR -- only one microwave source was necessary.

The stationary frequency microwaves were provided by a Sierra 201C generator whose output was amplified by an Alfred 5-6868 traveling wave tube amplifier. An HP8690B microwave sweeper equipped with an 8691A plug-in was the source of frequency swept microwaves. In general, both microwave sources were set to deliver equal power levels of 0.5-10 mW to the helix. Microwave frequency calibration was accomplished with a Beckman Transfer Oscillator (Model 540B) in conjunction with a HP5245L electronic counter.

The pulse sequences used for the two types of pulsed EEDOR experiments are shown in Figure 1. The timing sequence for c.w. EEDOR measurements is also included. A combination of commercial pulse generators and homebuilt TTL circuits created the pulse sequences of Figure 1 as voltages.

Pulses of microwaves were generated by the use of two HP PIN diodes (Model 33124) in each microwave line. When the microwaves were "off" the power reduction was at least 80 dB. Drivers used with the PINs turned on the microwaves when a 5 volt signal into 50 Ω was applied. Rise and fall times for the microwave power were no greater than 100 nsec.

When swept frequency pulsed EEDOR experiments were performed, a discriminator was used with the PM. The TTL compatible pulses generated when the discriminator detected an event passed through a gate which was only open during the time indicated in Figure 1a. Pulses which passed through the gate were integrated and converted to a voltage output which was then input to a Tracor Northern NS570A computer of averaged transients (CAT). At the end of each cycle of the pulse sequence the channel number of the CAT's memory was externally advanced by one unit. The externally driven CAT's sweep and the frequency swept microwaves were synchronized so that each of the first 512 channels of the memory corresponded to a certain frequency of the total microwave sweep of 8-10 MHz. At the end of the first 512 channels the pulses of stationary microwaves were inhibited and the sweep of the HP8690B was repeated. In this manner an unburned PMDR spectrum was accumulated in the remaining 512 channels of the CAT's memory. Repeated sweeps of the CAT were done in order to increase the signal-to-noise ratio.

The timing sequence shown in Figure 1a was repeated every 100 msec. This delay was chosen as a compromise between the time required for complete recovery of the triplet spin levels following the microwave pulses (~ 150 msec) and a desire to increase the duty cycle of the experiment. One full sweep of the CAT required just over a hundred seconds. Approximately one hundred sweeps were usually collected before outputting the data.

When stationary frequency pulsed EEDOR experiments were done the current generated by the PM tube was passed through a 100 kΩ resister and the resulting voltage was used as an input for the CAT. The CAT was triggered just before the start of the pulse sequence and swept internally at such a rate as to complete a sweep shortly after the single microwave pulse. The recorded signal in memory appeared as in Figure 2. The first sharp increase in intensity is due to the two microwave pulses separated by a time t' and the second is due to a single pulse. Delay times between the first two microwave pulses and the single pulse as well as between the single pulse and the start of a new cycle were sufficient to allow total recovery of the triplet spin levels.

Note that this experiment provides the same information as contained in one channel of the CAT during a swept frequency pulsed EEDOR experiment. The much higher repetition rate which can be used in the stationary frequency pulsed EEDOR experiment leads to a large increase in the accuracy of the data.

Most past EEDOR holeburning experiments have used two isolated helices in order to record continuous EEDOR spectra. In our experimental apparatus only one helix is used. In order to obtain a c.w. EEDOR spectra, the pulse sequence of Figure 1c was used for the microwaves. Since the pulse times are much less than the triplet spin level lifetimes, the microwaves behave as if they are on continuously. There are no interference effects between the two microwave sources since only one PIN diode is on at a time. In these experiments, photon counting detection was used with the ungated output of the integrater input to the CAT. Microwave powers were required to be ~ 100 times weaker than for the pulsed experiments in order to avoid saturation effects.

## 4. Experimental Results

Figures 3 and 4 show the results of swept frequency pulsed EEDOR experiments for the 2E spin transition of triplet TCB. The phosphorescence intensity change due to the microwaves is plotted as a function of the swept microwave frequency. For Figure 3, the delay time t between the stationary microwave pulse and the swept pulse was approximately .2 $\mu$sec. Microwave power levels were chosen to minimize the observed hole width. At higher powers, broadening was clearly evident in the hole width. Figure 3A shows the result when both pulses are applied to the sample. A narrow hole can be seen in the center of the band. In B only the swept microwave pulse was used. When part A was subtracted from part B and the resulting difference smoothed twice using a 3 point curve smoothing routine, the plot shown in part C was the result. The measured FWHM of the sharp band in part C is 190 kHz. Estimated error in this measurement is 50%. Large uncertainties arise due to noise in the signal and uncertainty in microwave calibration.

The curves shown in Figure 4 were recorded in exactly the same manner as those in Figure 3, with the exception that t was increased to 100 $\mu$sec. It is obvious by comparing the two figures that the hole burned in the inhomogeneous profile is shallower and much broader for the longer t. The difference of the burned and unburned bands yields a curve with a FWHM equal to 380 kHz.

Figure 5 shows the same holeburning curves for the c.w. EEDOR experiment. Note that the pulse sequence shown in Figure 1c was used. In this measurement the hole is barely visible. The FWHM of the band shown in Figure 5B is 2.8 MHz while the difference shown in Figure 5C gives a FWHM of 1.0 MHz. Clearly the apparent hole burned in the inhomogeneous profile when using pulsed excitation and short delay times is much sharper than when the system is allowed to equilibrate during a c.w. EEDOR experiment.

During the course of these experiments large variations were noted in the shapes and FWHM of the recorded inhomogeneous profiles. In all cases the bandshapes were asymmetric and were skewed to higher energy. Much of the variation in FWHM seems to be due to changes in the band shape from experiment to experiment. Variations of band FWHM have been observed before in triplet zero-field spin transitions(3) and such variations in bandshape for TCB have been alluded to.(4)

Another possible source of band variation arises from the use of a helix as a microwave slow wave device. The helix is supposed to act as a wide band microwave element,(25) but we did note some frequency effects in reflected power from helices used in these experiments and at times observed peculiar behavior in the spectral lineshapes. We attribute these observations to a frequency dependent impedance matching between the helix and coaxial line.

Single frequency pulsed EEDOR experiments were carried out using a microwave frequency (1.7443 GHz) chosen to maximize the intensity change due to the microwaves. Figure 2 shows the type of data which was recorded. Such data were analyzed by defining the ratio $R = \frac{A-B}{B}$. Here A is the intensity change due to the first two microwave pulses and B is the intensity increase due to the single pulse (see Figure 2). Increases in R as a function of t', the delay time between the first two pulses, reflect the filling and spreading of the hole as spectral diffusion occurs.

Figure 6 is a plot of R versus t' recorded during several experiments. Data recorded during one experiment gave a curve with much less variation. We attribute differences between experiments to minor fluctuations in the microwave power being applied to the sample.

The behavior of R shown in Figure 6 was typical of all experiments. As t' was increased from .2 μsec to 20 μsec there was a very fast partial recovery of the hole. This recovery was extremely fast at short t' but then fell off in rate. After 20 μsec the recovery of the hole became very slow. Experiments with t' as long as 5 msec indicated that the slow recovery was still continuing. The value of R at t' = 5 msec was approximately .8 after correction for vertical processes.

It was extremely encouraging to note that both types of pulsed EEDOR experiments gave equivalent results. Values of R measured from the swept frequency experiment as a function of t gave the same behavior as those recorded in stationary experiments as a function of t'. Values of R were also in close agreement and phosphorescence intensity changes due to the microwave pulses were of the same magnitude.

By performing the experiments at 1.5 °K and 4.2 °K it was possible to show that the results were temperature independent over this range. The rate of the spectral diffusion was found to be independent of exciting light intensity (various triplet concentrations in the crystal) as well as of TCB. This suggests that the observed diffusion is not a result of cross-relaxation between different triplet spin systems or triplet-triplet electronic energy transfer processes.

## 5. Discussion

The experimental results described in the last section prove conclusively that spectral diffusion does occur for the spin levels of phosphorescent triplets and indicate that this is the source of the homogeneous lineshapes for these magnetic resonance transitions. Furthermore, there are clearly two time domains for the diffusion. The faster of the two is the source of echo decay behavior while the longer results in the extreme broadness of the hole burned when using c.w. microwave excitation for the EEDOR experiment.

Before discussing the origin of the two diffusion times it is necessary to note several important factors concerning the pulsed EEDOR method. An awareness and understanding of such factors is essential to the successful analysis of pulsed EEDOR experiments.

The strong spin alignment often found in triplet states at liquid helium temperatures coupled with the sensitivity of optical detection is a decided advantage in performing these experiments. However, this advantage is somewhat overcome by the necessity of selecting a narrow portion of the total available inhomogeneous profile of the magnetic resonance transition and for using detection gating. A further loss of signal-to-noise ratio occurs due to the necessity of waiting for the spin levels to recover before a pulse sequence can be repeated. These limitations are the basic reason for the noise in the signals shown in Figures 3 and 4.

In past pulsed EEDOR experiments the applied microwave powers were such that the holes burned in the inhomogeneous profile were much greater than the width of a homogeneous packet. For the work described here it was desirable to only excite molecules within the homogeneous width. An estimate of the maximum microwave magnetic field ($H_1$) which can be used has been obtained by using equivalent equations developed by Mims et al.(19) and Breiland et al.(8) to give the behavior of spins in an inhomogeneous profile when a microwave field of strength $H_1$ at frequency $\omega_0$ is applied. These equations can be rewritten in terms of the spin populations in the two spin levels before the field is applied and yield the behavior of the spin populations as a function of time during the pulse. When written in terms of the $\tau_A$ and $\tau_B$ spin level populations of TCB the equations become

$$N_{AB}(t,\omega) = N_{AB}(0,\omega) \frac{1}{\Delta\omega^2 + \omega_1^2} \left(\Delta\omega^2 + \omega_1^2 \cos\left[(\Delta\omega^2 + \omega_1^2)^{1/2} t\right]\right). . . \quad (1)$$

$N_{AB}(t,\omega)$ is the difference in the number of spins in the $\tau_A$ and $\tau_B$ spin levels having an angular frequency of $\omega$; t is the time since the start of the microwave pulse. $\Delta\omega = \omega_0 - \omega$ and $\omega_1 = \gamma H_1$ where $\gamma$ is the magnetogyric ratio of the electron. This function is derived by assuming the spins follow $H_1$ coherently. After a period of time this condition will not be met since dephasing events will occur, but Mims et al.(19) have found that the hole shape indicated by Equation 1 is still approximately valid even when coherence is lost.

The hole widths derived from this equation have a FWHM on the order of $2\gamma H_1$. The fraction of population transferred from $\tau_A$ to $\tau_B$ at a frequency $\omega_0$ can be determined using the formula $\gamma H_1 t = \phi$ where $\phi = \pi/2$ radians corresponds to saturation at $\omega_0$ while $\phi = \pi$ radians indicates inversion of the spin level populations. These equations assume the spin transitions follow $H_1$ coherently. Obviously, at long t this will not be true and the equation will no longer be valid. Homogeneous FWHM are given approximately by $\frac{2}{T_2}$ where $T_2$ is the 1/e time measured in an echo experiment. In order for power broadening to be less than the homogeneous width it is required that $\frac{2}{T_2} > 2\gamma H_1$ which implies $\frac{t}{T_2} > \phi$. The last inequality offers an indication of the amount of population which will be transferred during a pulse of period t which insures power broadening to be less than the homogeneous linewidth. For $\phi = 90°$ one finds $t > \frac{\pi}{2} T_2$. In our experiments we wished to insure that the spins at $\omega_0$ were saturated (to maximize the signal) so a pulse of 10 μsec was used and $t \approx 2.5\ T_2$. Note that this requirement places a fundamental limit on the time resolution of the experiment. Using Equation 1 and assuming $\gamma H_1 t = \pi/2$ the calculated lineshape (which is not Lorentzian) has a frequency FWHM of 88 kHz which nearly equals the FWHM predicted for the homogeneous line on the basis of its measured $T_2$ time.

We have not as yet mentioned an important problem in the determination of the FWHM of the burned hole created by a pulsed EEDOR experiment. In the experiments performed in this work a microwave pulse is used to create the hole and a second pulse is used to monitor its width. Both pulses will sample a frequency range within the inhomogeneous profile. Each burns a hole and the resulting signal gives an apparent FWHM for the hole greater than that actually created by the holeburning (stationary frequency) microwave pulse. A similar problem has been considered by Voelker et al.(27) for the case of photochemical holeburning in the $S_1 \leftarrow S_0$ transition of free base porphyrin.

A computer simulation was performed in order to determine the effect of the convolutions of these two transitions on the observed hole FWHM. For this simulation the inhomogeneous line shape was assumed to be a Gaussian with a FWHM of 2 MHz. A microwave pulse applied at $\omega_0$ was designed to saturate the transition at a frequency of $\omega_0$. The fractional change of population fell off as a Lorentzian function of frequency with a FWHM of 125 kHz. Spectral diffusion processes are assumed absent. In an exact mimic of the experiment a population distribution was calculated following the first pulse and then a frequency swept pulse of the same power was applied at various frequencies across the inhomogeneous profile. The resulting calculated intensity changes were then output. Figure 7 shows the burned curve (A), the unburned curve (B), and the difference of the two (C) calculated in this manner. The FWHM of the difference of (A) and (B) was 250 kHz. These calculations indicate that the actual width of the hole burned in the inhomogeneous profile is one-half of the band which results when the difference between the burned and unburned spectra is taken. This will be true as long as the inhomogeneous width is considerably greater than the homogeneous. Note that these calculations reveal the necessity of comparing both the burned and unburned spectra. In past holeburning measurements of triplet spin transitions this was not done.

The calculations above suggest that the FWHM of the hole burned in the inhomogeneous spin transition profile of TCB when t equals .2 μsec (see Figure 3) is one half of 190 kHz or 95 kHz. Other measurements have yielded similar values. Note that the shape of the hole cannot be determined due to the noise in the spectra.

The FWHM of the hole measured from time resolved holeburning is very close to the value predicted based on the $\frac{1}{e}$ time for the spin echo decay in the same system -- 80 kHz. This observation is somewhat surprising due to the fact that 10 μsec microwave pulses were used and single frequency pulsed EEDOR experiments indicate that spectral diffusion is very fast on a μsec time scale. Spectral diffusion could be expected to broaden the burned hole during the pulses, but the experimental results seem to indicate that spectral diffusion was inhibited during the time when the microwaves were on. It is impossible for us to offer a theoretical interpretation of this result at the present time. Further experimental and theoretical studies are obviously required. The difficulty might arise from our assumption that we are measuring a width which corresponds to the one calculated from the spin-echo results. This might not be true due to one of two reasons. The first is the fact that the two experiments are carried out in two different time scales and thus could sample different frequency components of the local field. The second is the fact that even at the lowest power we have used, we are affecting the population of molecules outside the spin-echo corresponding width.

There have been several attempts to develop theories describing spectral diffusion in electronic spin systems.(28-31) However, there has been no work known to us where the interactions of triplets in zero field and surrounding nuclei have been considered. For this reason possible sources of spectral diffusion will be discussed in a qualitative and descriptive manner.

It seems fairly clear that the initial fast spectral diffusion is due to fluctuating magnetic fields at the TCB triplet arising from magnetic nuclei (protons) on the surrounding host durene molecules. Several workers have previously reached the same conclusion.(4,5,7,8)

Interesting comparisons can be made between the spectral diffusion results observed for the triplet and the early work of Mims et al.(19) These workers showed that the spin echo decay of $Ce^{+3}$ could be fit by a decay envelop proportional to $\exp(-m\tau^2)$ where m is the spin diffusion parameter for a Lorentzian diffusion kernel.(19) This form has also been observed by Brown(17) for organic radicals isolated in glasses. Significantly, the $\frac{1}{e}$ times for echo decay in the organic systems were very similar to those which have been measured for triplets. If one assumes that the triplet spin echo decay obeys the same expression and the 1/e time of 4 μsec determined previously is used,(8) m is calculated to be $9 \times 10^{10}$ $\sec^{-2}$. Mims et al. demonstrated that this value of m could be used to calculate the rate of filling in of the hole at $\omega_0$ following a microwave pulse.(19) When modified to give an equation in terms of the R defined earlier in this work, their expression becomes

$$R = 1 - R_o\left(1 + \frac{mt'}{\Gamma}\right)^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$R_o$ is the value of R at the end of the first pulse, t' is the time between the two pulses as defined earlier, and Γ is the FWHM of the hole burned in the inhomogeneous profile. For the case of the inorganic ions(19) it was found that spectral diffusion was capable of completely filling in the hole. In our experiments this would mean that R would very quickly increase to a value of 1. However, the experimental results indicate that it rapidly rises from a value of $R_o \approx .33$ and then slows dramatically at $R \approx .50$ after approximately 25 μsec. We interpret the difference between the two experiments as indicating that the rapid spectral diffusion can only occur over a limited frequency range in triplet spin systems. Based on swept frequency pulsed EEDOR experiments, this frequency range is estimated to be approximately two times greater than the homogeneous width. That interaction with surrounding nuclei might modify the frequencies of triplet spin states in zero field only slightly is consistent with the weak hyperfine interactions expected between a triplet and magnetic nuclei in zero field.(3)

The above reasoning can be tested in a crude manner by assuming that on the time scale of the rapid spectral diffusion the slower process is a constant. Such an assumption allows Equation 2 to be rewritten as

$$R = R' - R_o (1 + mt'/\Gamma)^{-1} \quad . . . . . . . . . . . . . . . \quad (3)$$

R' is the limiting value of R. Such an equation is a crude approximation since it does not account for the fact that the frequency range of the rapid diffusion is limited.

The solid curve shown in Figure 6 is the result when R' is set to .52 and Γ to 90 hHz. Clearly, this curve gives good agreement with experiment. Experiments with t' less than 1 μsec also yield good agreement with the predictions of Equation 3.

It is very difficult to determine with certainty the origin of the slower spectral diffusion. However, an educated guess can be made. We have demonstrated that the inhomogeneous broadening of the triplet spin transitions due to the interaction of the triplet and nuclei on surrounding host molecules is on the order of 200 kHz. This requires that the remainder of the inhomogeneous broadening is due to other sources. Two possibilities are hyperfine interaction of the triplet spin and the magnetic nuclei on the same molecule and the existence of different sites in the crystal due to strain effects which can modify the frequencies of the triplet spin transitions. Hutchison *et al.*(3) have shown that the zero-field spectral lineshapes of naphthalene in durene can be explained quite adequately by assuming that the hyperfine interactions between triplet spins and nuclei on the same molecule are the primary source of the inhomogeneous broadening. For this system the bandshapes were nonsymmetrical and on the order of 1.5 - 2.2 MHz in FWHM. By comparison of TCB's inhomogeneous profile with that of naphthalene, it would appear that most of the broadening for TCB is due to the same source. Schuch and Harris have reached a similar conclusion.(4)

The energy of a spin transition will be changed when a nuclei on the triplet molecule changes state. Such spin flips at the proper rate would result in the slow spectral diffusion observed and would be able to cover most of the observed inhomogeneous profile. The spin flips of the nuclei might arise due to spin lattice relaxation (the temperature independence of the results argues against this) or spin-spin interactions between nuclei. Such a mechanism for the slow spectral diffusion is very appealing, but it must be noted that other workers have previously concluded that such changes in the nuclear spin states in the same system occur at a rate smaller than one half of the average triplet sublevel decay rates.(4) The true origin of the slow diffusion may not be discovered until further experiments are performed and theories are developed which describe spectral diffusion for triplet states in zero field.

## 6. Concluding Remarks

Pulsed EEDOR techniques have been developed which utilize optical detection of triplet state spin transitions to study spectral diffusion. As previously predicted based on spin echo experiments, a rapid spectral diffusion process has been found. This spectral diffusion is very limited in the range of frequencies it can sample within the inhomogeneous profile of the spin transition and is attributed to the weak zerofield interactions between the isolated triplet molecule and nuclei on surrounding host molecules.

A second type of spectral diffusion has been identified which occurs much more slowly, but which is capable of generating much larger changes in triplet spin level transition energies. This slow diffusion limits the holewidth observed in c.w.EEDOR holeburning experiments. This spectral diffusion has been tentatively attributed to interactions between the triplet spin states and nuclear spin states located on the same molecule.

At this time it is clear that the processes which result in spectral diffusion within zerofield triplet spin transitions are not well understood. We are not aware of any theories which treat such spectral diffusion. The results of this work should provide an impetus for theoretical developments to describe the dynamic interaction of triplet spin states and surrounding nuclear spin states in zero field.

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## REFERENCES

1. E. L. Hahn, Phys. Rev. 80 (1950) 580.
2. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73 (1948) 679.
3. Clyde A. Hutchison, J. V. Nicholas, and G. W. Scott, J. Chem. Phys. 53 (1970) 1906.
4. H. Schuch and C. B. Harris, Z. Naturforsch. 30a (1975) 361.
5. J. Schmidt, Chem. Phys. Letters 14 (1972) 411.
6. W. G. Brieland, C. B. Harris, and A. Pines, Phys. Rev. Letters 30 (1973) 158.
7. B. J. Botter, D. C. Doetschman, J. Schmidt, and J. H. van der Waals, Mol. Phys. 30 (1975) 609.
8. W. G. Breiland, H. C. Brenner, and C. B. Harris, J. Chem. Phys. 62 (1975) 3458.
9. M. Leung and M. A. El-Sayed, Chem. Phys. Letters 16 (1972) 454.
10. J. Zuclich, J. U. von Schutz and A. H. Maki, J. Amer. Chem. Soc. 96 (1974) 710.
11. J. U. von Schutz, J. Zuclich, and A. H. Maki, J. Amer. Chem. Soc. 96 (1974) 714.
12. A. J. Hoff, Biochim. Biophys. Acta 440 (1976) 765.
13. R. H. Clarke and R. E. Connors, Chem. Phys. Letters 42 (1976) 69.
14. J. U. von Schutz and W. Dietrich, Chem. Phys. Letters 51 (1977) 418.
15. K. W. Rousslang, J. B. A. Ross, D. A. Derauleau, and A. L. Kwiram, Biochemistry 17 (1978) 1087.
16. N. Nishi, J. Schmidt, A. J. Hoff, and J. H. van der Waals, Chem. Phys. Letters 56 (1978) 205.
17. I. M. Brown, J. Chem. Phys. 55 (1971) 2377.
18. T. S. Kuan, D. S. Tinti, and M. A. El-Sayed, Chem. Phys. Letters 4 (1970) 507.
19. W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. 123 (1961) 2059.
20. C. R. Chen and M. A. El-Sayed, Chem. Phys. Letters 10 (1971) 307.
21. A. H. Francis and C. B. Harris, J. Chem. Phys. 57 (1972) 1050.
22. W. M. Pitts and M. A. El-Sayed, Chem. Phys. 19 (1977) 289.
23. M. D. Fayer and C. B. Harris, Chem. Phys. Letters 25 (1974) 149.

24. H. C. Brenner, J. C. Brock, and C. B. Harris, J. Chem. Phys. 60 (1974) 4448.

25. R. H. Webb, Rev. Sci. Ins. 33 (1962) 732.

26. J. M. Robertson, Pro. Roy. Soc. 142 (1933) 659.

27. S. Voelker, R. M. Macfarlane, A. Z. Genock, and H. P. Trommsdorff, J. Chem. Phys. 67 (1977) 1759.

28. W. B. Mims, Phys. Rev. 168 (1968) 370.

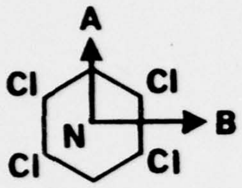
29. J. R. Klauder and P. W. Anderson, Phys. Rev. 125 (1962) 912.

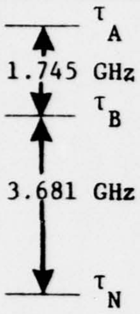
30. P. Hu and S. R. Hartman, Phys. Rev. B9 (1974) 1.

31. P. Hu and L. R. Walker, Phys. Rev. B18 (1978) 1300.

Table 1

RELEVANT PROPERTIES OF TETRACHLOROBENZENE IN DURENE AT 1.6 K





| Spin level | Relative $K^0$ | $k^0(s^{-1})$ | Relative [39] $r_k^0(0,0)$ | Relative [39] $r_k^0(0,234\ cm^{-1})$ |
|---|---|---|---|---|
| $\tau_N$ | 0.195 | 1.43 | 0.2 | 0.1 |
| $\tau_B$ | 1.0 | 29.10 | 19.0 | 3.7 |
| $\tau_A$ | 3.8 | 27.78 | 0.0 | 17.0 |

## FIGURE CAPTIONS

Fig. 1 The microwave and photon counting gating sequences for the a) swept frequency pulsed EEDOR, b) stationary frequency pulsed EEDOR, and c) "CW" EEDOR.

Fig. 2 An example of the recorded behavior of phosphorescence intensity during a stationary frequency pulsed EEDOR experiment. The increase in phosphorescence intensity due to the first two microwave pulses is denoted by A while the intensity increase due to the single microwave pulse is B. R is defined as $\frac{A-B}{B}$.

Fig. 3 The results of a swept frequency pulsed EEDOR experiment with $t = 0.2$ μsec. Part (A) shows the observed transition when only the swept microwave pulse is applied to the 2E transition of TCB. In (B) the stationary microwave pulse has been used and a hole has been burned in the spectral profile. Part (C) shows twice the difference of parts (A) and (B). A sharp spike can be seen in the difference corresponding to the burned hole.

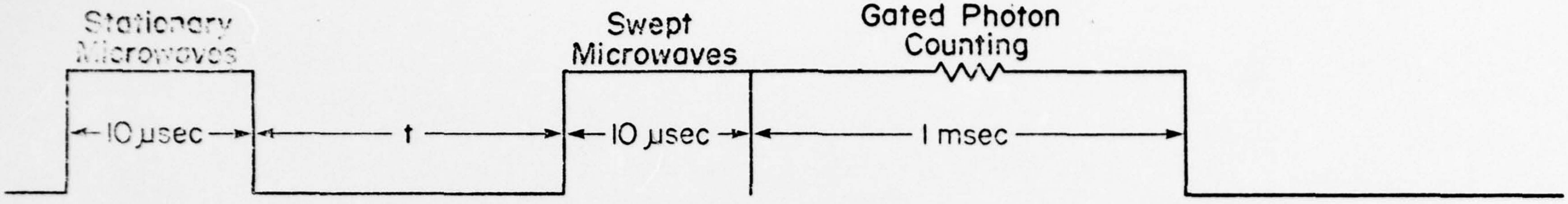
Fig. 4 The results of a swept frequency pulsed EEDOR experiment performed in exactly the same manner as in Fig. 3 except that t has been increased from 0.2 μsec to 100 μsec. By comparing the two figures it is clear that the longer delay results in a much broader and shallower hole.

Fig. 5 The results of a "CW" EEDOR experiment. Note that the burned hole in (B) is barely visible but (C) shows that a very large portion of the inhomogeneous profile has been burned by the stationary microwaves.

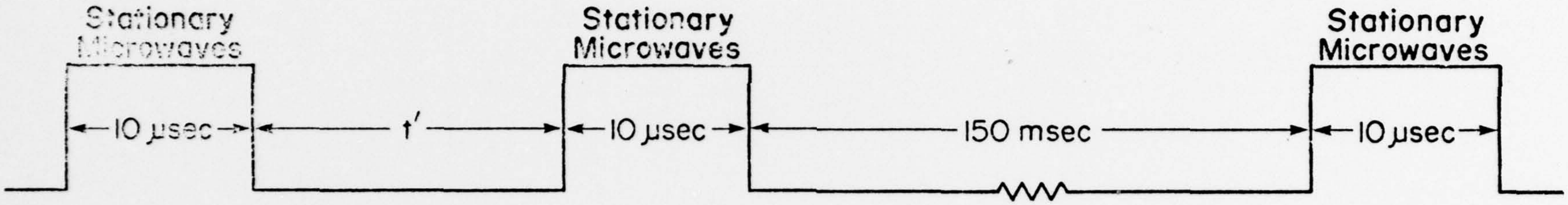
Fig. 6 Experimental values of R plotted against t', the time between the first and second pulses in the stationary frequency pulsed EEDOR experiment. The solid line is the calculated curve obtained when Equation 3 is used.

Fig. 7 The results of a computer simulation for a swept frequency pulsed EEDOR experiment. The inhomogeneous line was chosen to have a FWHM of 2 MHz while the homogeneous FWHM is 125 kHz. The difference of parts (A) and (B) shown in part (C) has a FWHM of 250 kHz.

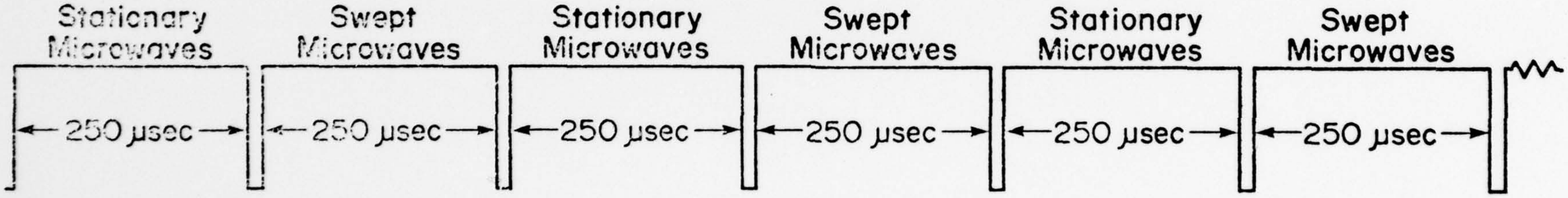
a) Swept Frequency Pulsed EEDOR

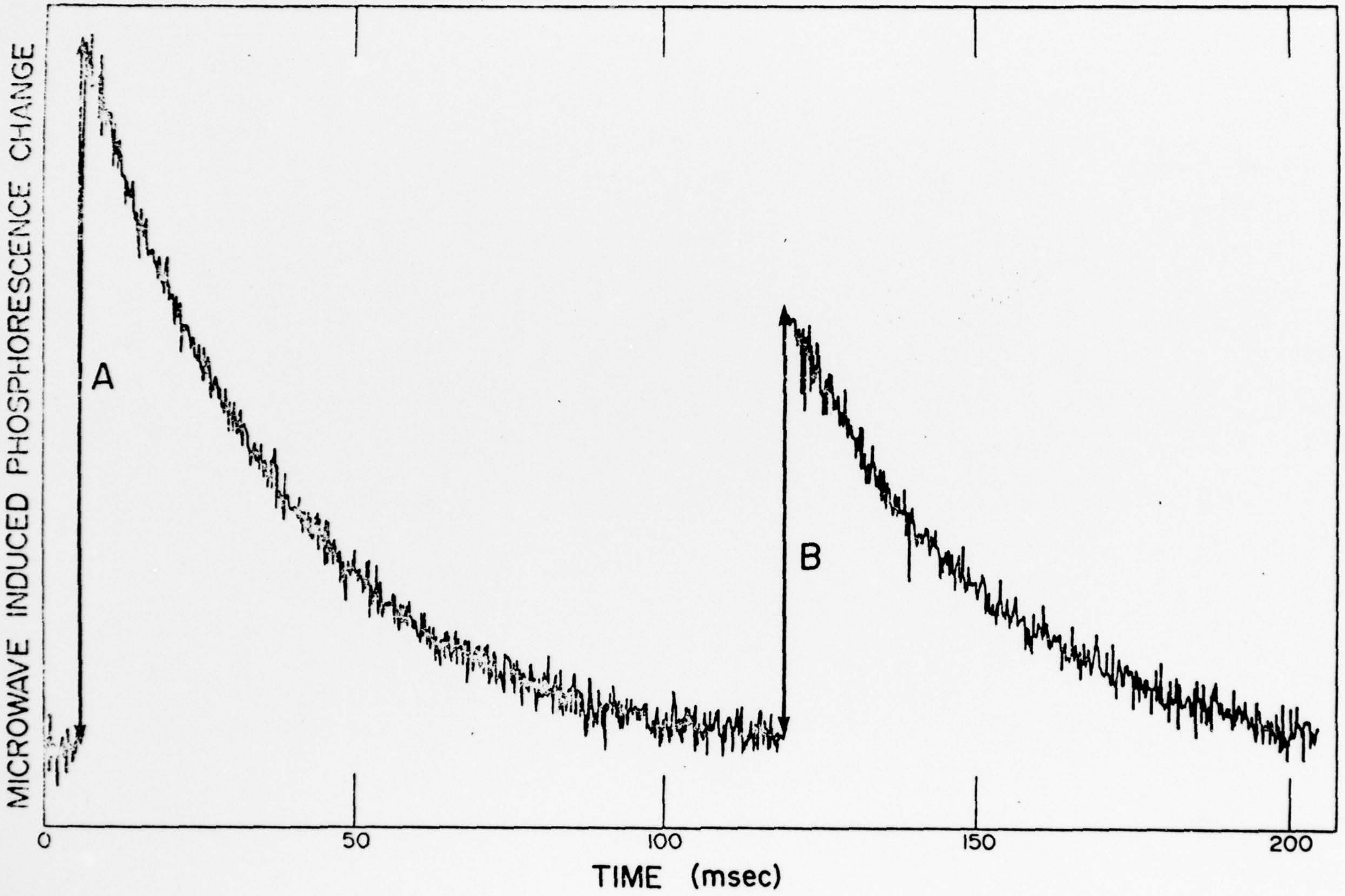


b) Single Frequency Pulsed EEDOR

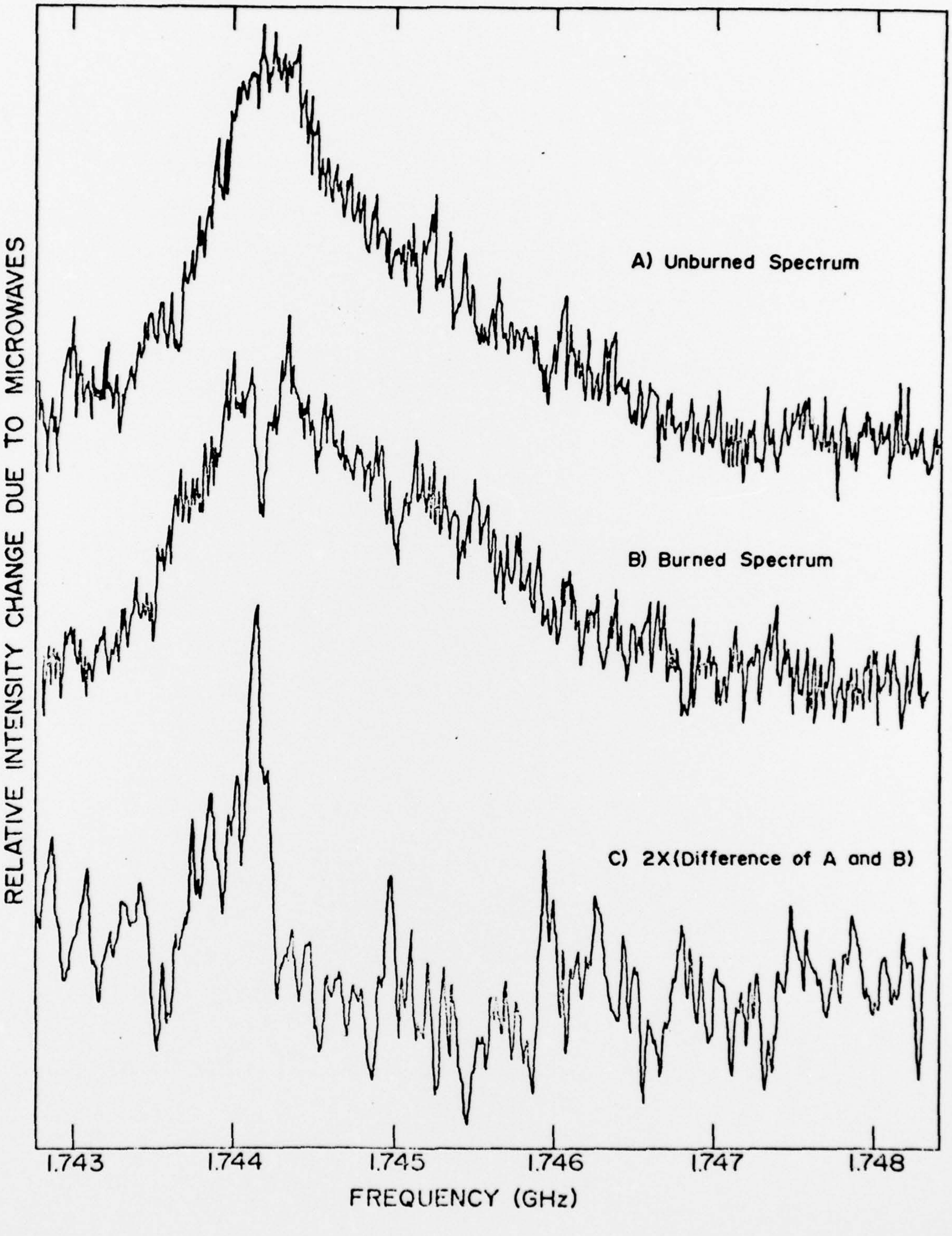


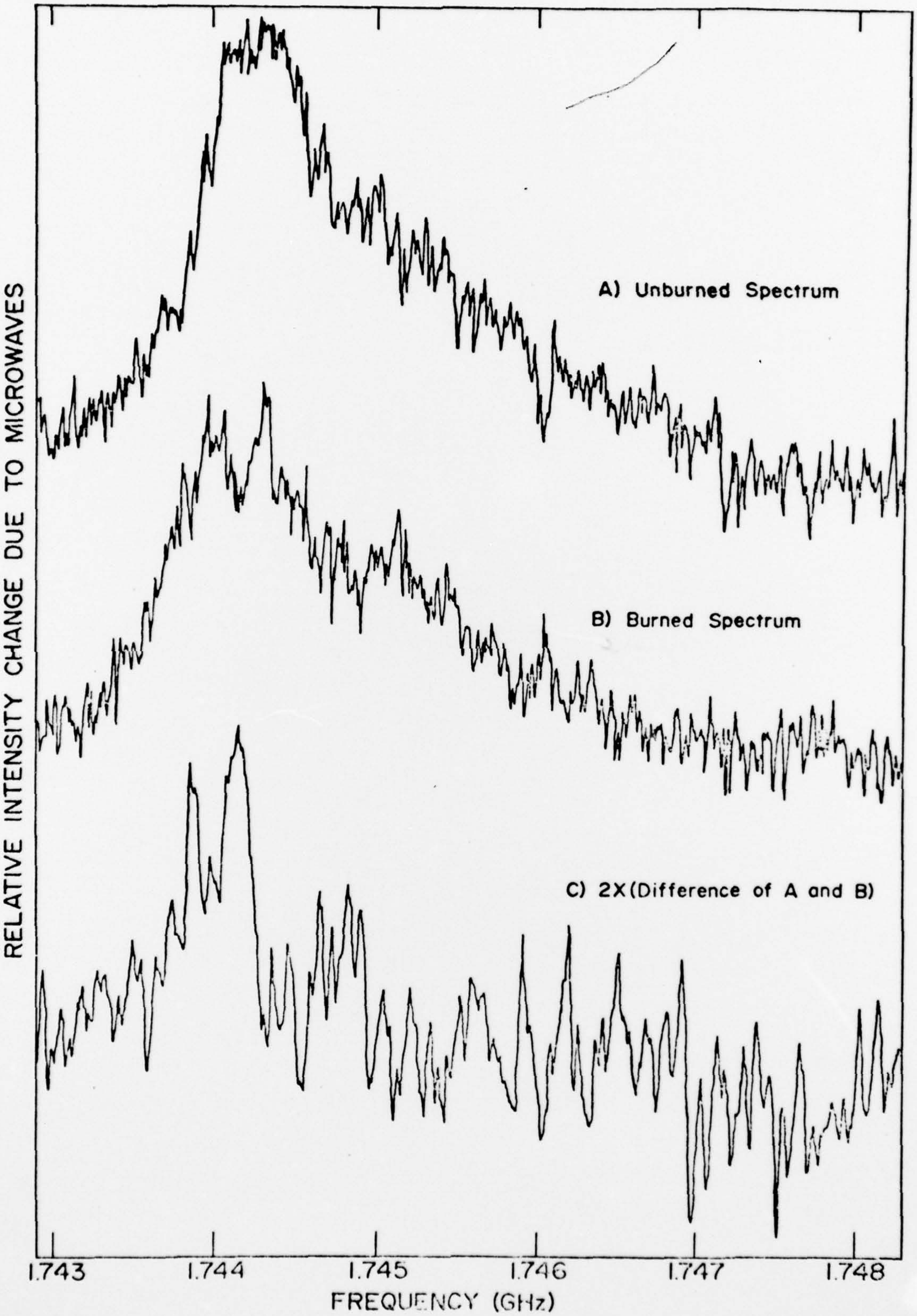
c) "CW" EEDOR



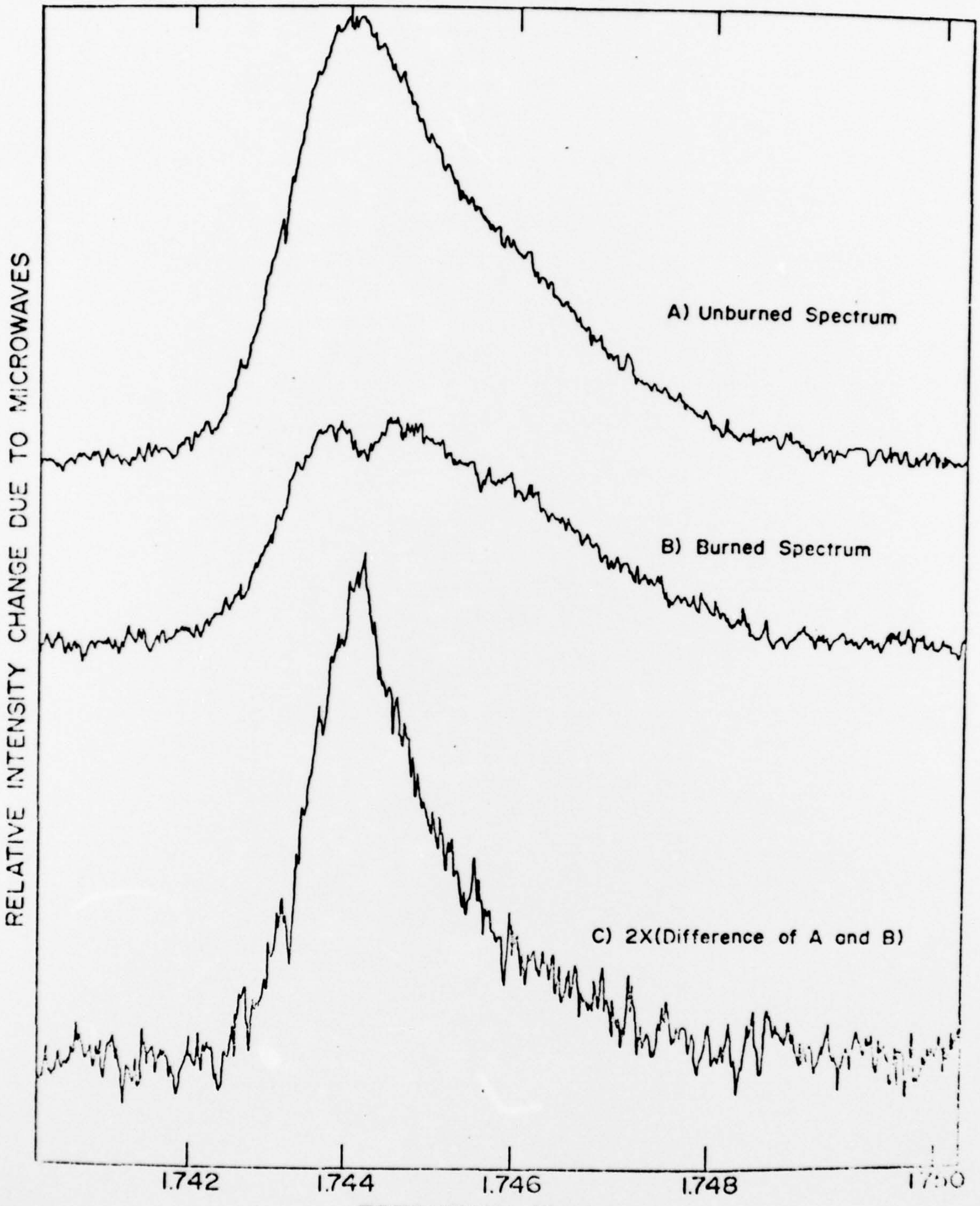

MICROWAVE INDUCED PHOSPHORESCENCE CHANGE
A
B
0
50
100
150
200
TIME (msec)

②

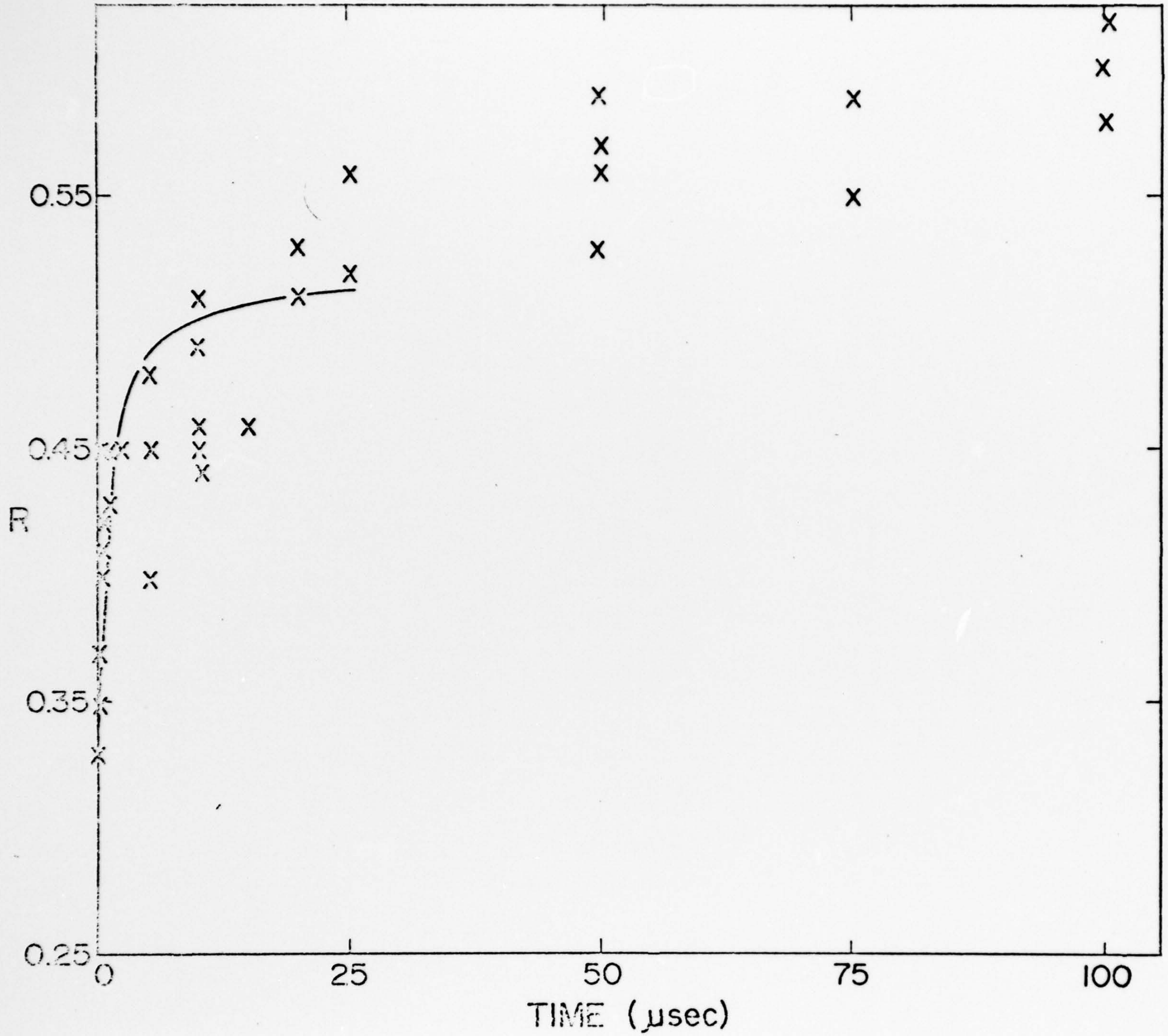

RELATIVE INTENSITY CHANGE DUE TO MICROWAVES
A) Unburned Spectrum
B) Burned Spectrum
C) 2X(Difference of A and B)
1.743
1.744
1.745
1.746
1.747
1.748
FREQUENCY (GHz)

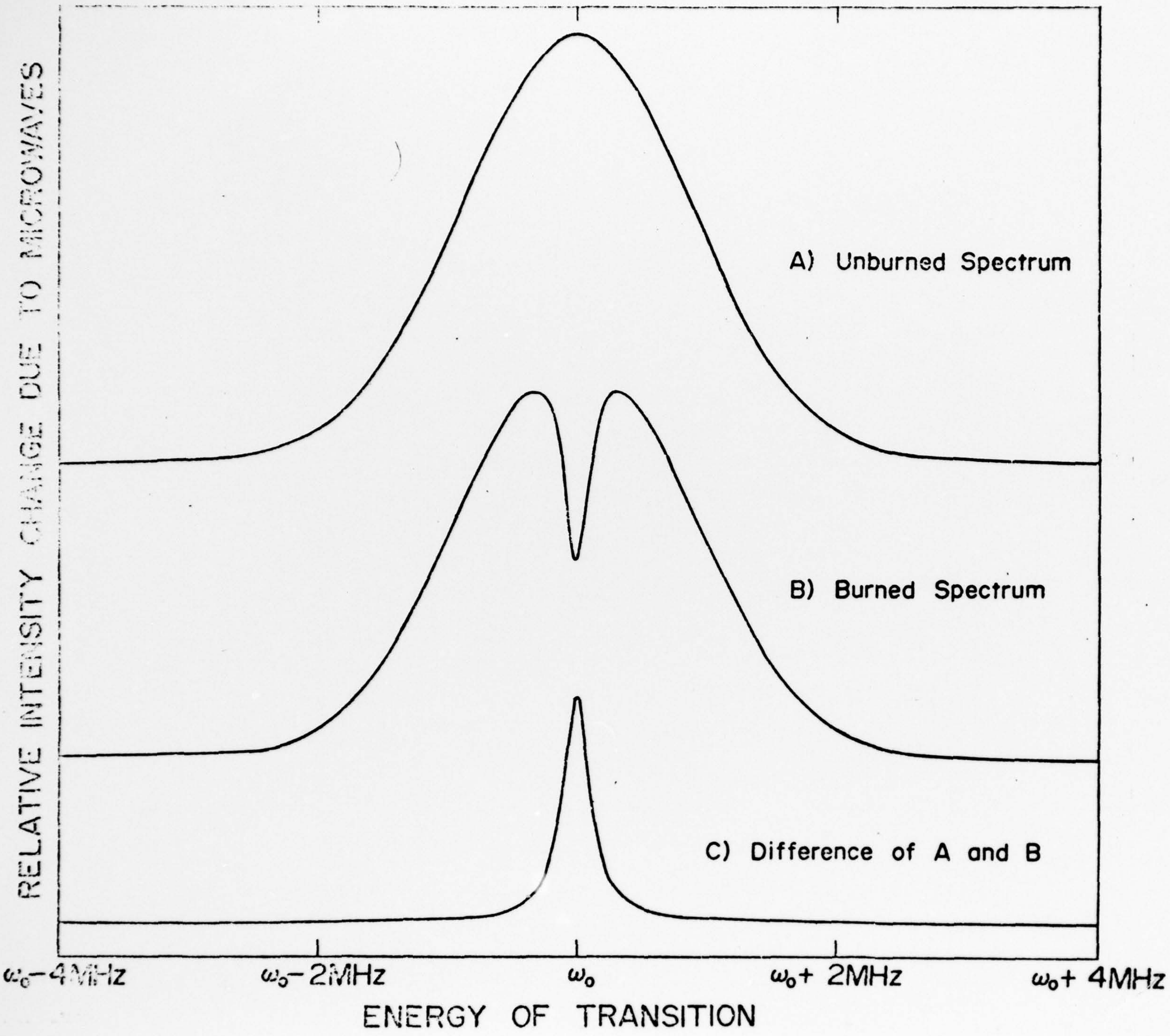

RELATIVE INTENSITY CHANGE DUE TO MICROWAVES
A) Unburned Spectrum
B) Burned Spectrum
C) 2X(Difference of A and B)
1.743
1.744
1.745
1.746
1.747
1.748
FREQUENCY (GHz)

4


RELATIVE INTENSITY CHANGE DUE TO MICROWAVES
A) Unburned Spectrum
B) Burned Spectrum
C) 2X(Difference of A and B)
1.742
1.744
1.746
1.748
1.750
FREQUENCY (GHz)

⑤


R
0.55
0.45
0.35
0.25
0
25
50
75
100
TIME (μsec)


A) Unburned Spectrum
B) Burned Spectrum
C) Difference of A and B
RELATIVE INTENSITY CHANGE DUE TO MICROWAVES
$\omega_o - 4$MHz
$\omega_o - 2$MHz
$\omega_o$
$\omega_o + 2$MHz
$\omega_o + 4$MHz
ENERGY OF TRANSITION

③

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