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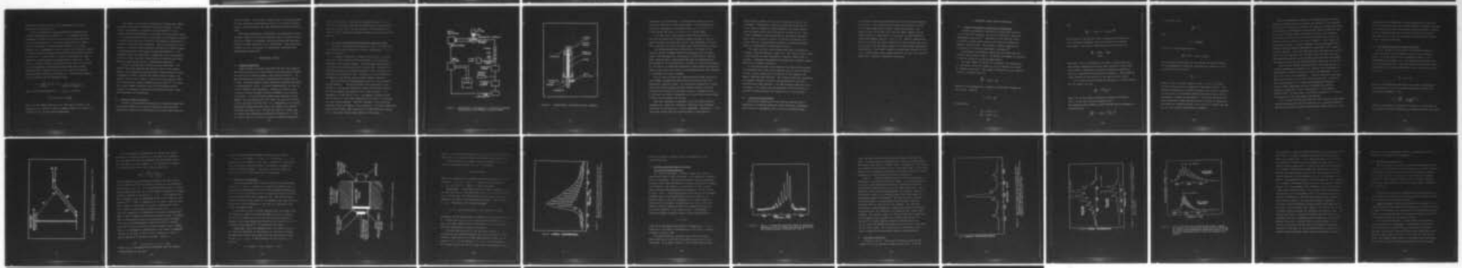

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OPTICAL DETECTION OF ULTRASOUND IN PARAMAGNETIC CRYSTALS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE
CHICAGO, ILLINOIS 60680

MAY 1976

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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Project Engineer

FOR THE COMMANDER

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Optical detection methods were employed to investigate the interaction of applied coherent phonons with the excited state spin system of molecular crystals. Results are reported and discussed concerning both single and double quantum resonant interactions as well as phonon-nuclear quadrupole interactions and non-resonant spin-phonon interactions.

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FOREWORD

The objectives of the contracted research were to demonstrate the optical detection of acoustic paramagnetic resonance in electronically excited triplet metastable states of organic molecules and to explore the usefulness of the optical detection method as a possible incoherent detector for ultrasonic phonons. These objectives have been largely accomplished and the results are covered in detail in the present report. The main body of this report is concerned with characterization and evaluation of optically detected acoustic paramagnetic resonance in solids. The major portion of the experimental and theoretical investigation was carried out by Dr. A. I. Attia and reported in his doctoral dissertation from which the majority of the text of this report has been directly taken. Portions of this work have been reported in the published literature[1] and have been reviewed in professional periodicals.[2] Some of the textual material in this report has been taken directly from these sources.

This report was prepared under Project 7353, Task 735308, Contract F33615-73-C-5048.

ABSTRACT

Results of an experimental investigation are presented concerning the interactions which occur between coherent phonons, and molecules optically pumped to the first excited triplet state in a molecular crystal lattice.

Coherent phonon induced transitions were investigated using ZnO piezoelectric transducers for the generation of longitudinally polarized hypersonic waves. The optically detected acoustic paramagnetic resonance of the metastable triplet state of 1,2,4,5-tetrachlorobenzene in zero field as well as an acoustic resonance signal induced by an off resonance acoustic field are reported; this last effect is attributed to the inelastic scattering of phonons, due to phonon-defect and phonon-phonon interaction, into the bandwidth of the spins. Two-phonon induced EPR transitions and nuclear quadrupole effects are also reported and discussed. Additionally, preliminary results are presented which indicate that two factors are of critical importance in the observation of optically detected acoustic resonance in molecular crystals: the concentration of paramagnetic centers and the density of defects.

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1. INTRODUCTION

In 1949 Bitter[3] called attention to the possibility of the optical detection of a radiofrequency resonance of an excited atom. Brossel and Kastler[4] suggested a study of the modulation of the emission intensity from the excited state of an atom provided a state of spin alignment exists. That suggestion was quickly followed by Brossel and Bitter[5] using the 6 $^3P_1$ state of the mercury atom in the vapor phase. Excitation of the 6 $^3P_1$ state was accomplished by optical resonance radiation with polarized light to provide the initial inequality of population in the Zeeman pattern of the excited state. The degree of polarization of the emission was altered by absorption of radiofrequency radiation. Following that initial experiment, double resonance experiments of a similar nature were conducted on a number of excited state species in the gas phase.[6]

Similar experiments were soon executed in the solid state. Geschwind, Collins and Schawlow[7] observed paramagnetic resonance in an excited metastable state of Cr^{+3} in Al_2O_3 at 1.6 °K. In contrast to standard optical double resonance techniques in gases, where normally a change in linear or circular polarization is detected along the field direction, selective reabsorption in the ground state Zeeman levels of the fluorescent light from the excited state of Cr^{+3} enabled the authors to observe a change in the light in linear polarization in a direction perpendicular to the field. In 1967 Sharnoff[8] and Kwiram[9] carried out successful magnetic resonance experiments on photoexcited triplet state organic molecules in the solid state at low temperatures (see Figure 1).

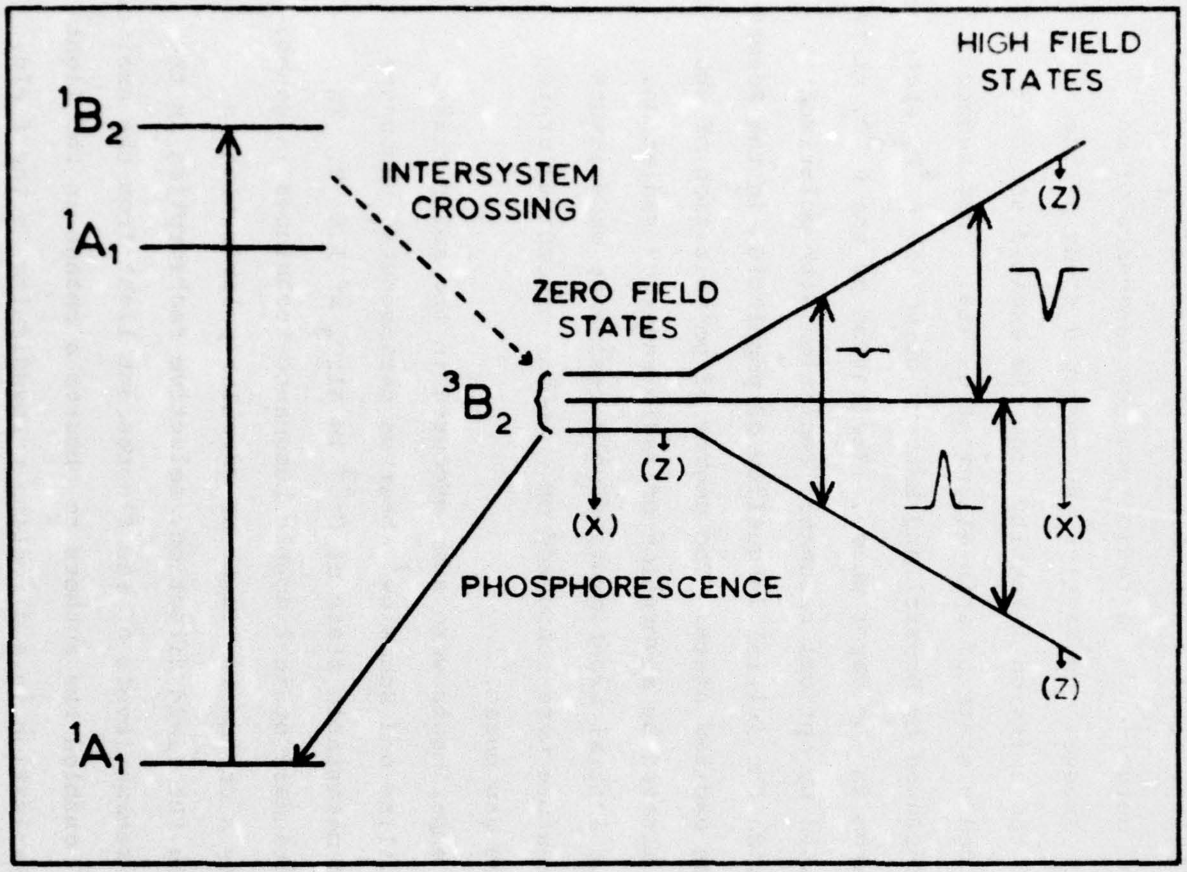

Figure 1 Electronic States of Phenanthrene Showing Details of the Triplet State in Zero Field and in the Presence of a Magnetic Field

Briefly, there is an initial inequality in the population of the magnetic sublevels of the triplet state; the net effect of the transition induced by the oscillating magnetic field is to change this inequality and therefore to modify any property depending on it, such as the level of phosphorescence intensity.

1.1 The Triplet State

When considering the kinetics of triplet relaxation, it is important to recall that depending on the symmetry of the state, the triplet state may consist of three non-degenerate spin states even in the absence of a magnetic field; the magnetic dipole-dipole forces between the two unpaired electrons remove the degeneracy of the triplet sublevels. We represent this fact diagrammatically in Figure 2. In molecules containing atoms of large nuclear charge, spin-orbit interactions could lead to significant contributions to the splitting.

The relaxation processes between the zero field levels at temperatures around 77 °K are much faster than the corresponding phosphorescent processes. Below 4.2 °K the spin-lattice relaxation processes could be slower than the phosphorescence from the individual zero field levels. The individual radiative decay constants for the spin states may differ by an order of magnitude or more.

If excitation and deactivation of different zero field levels are taking place continuously, a non-Boltzmann distribution may

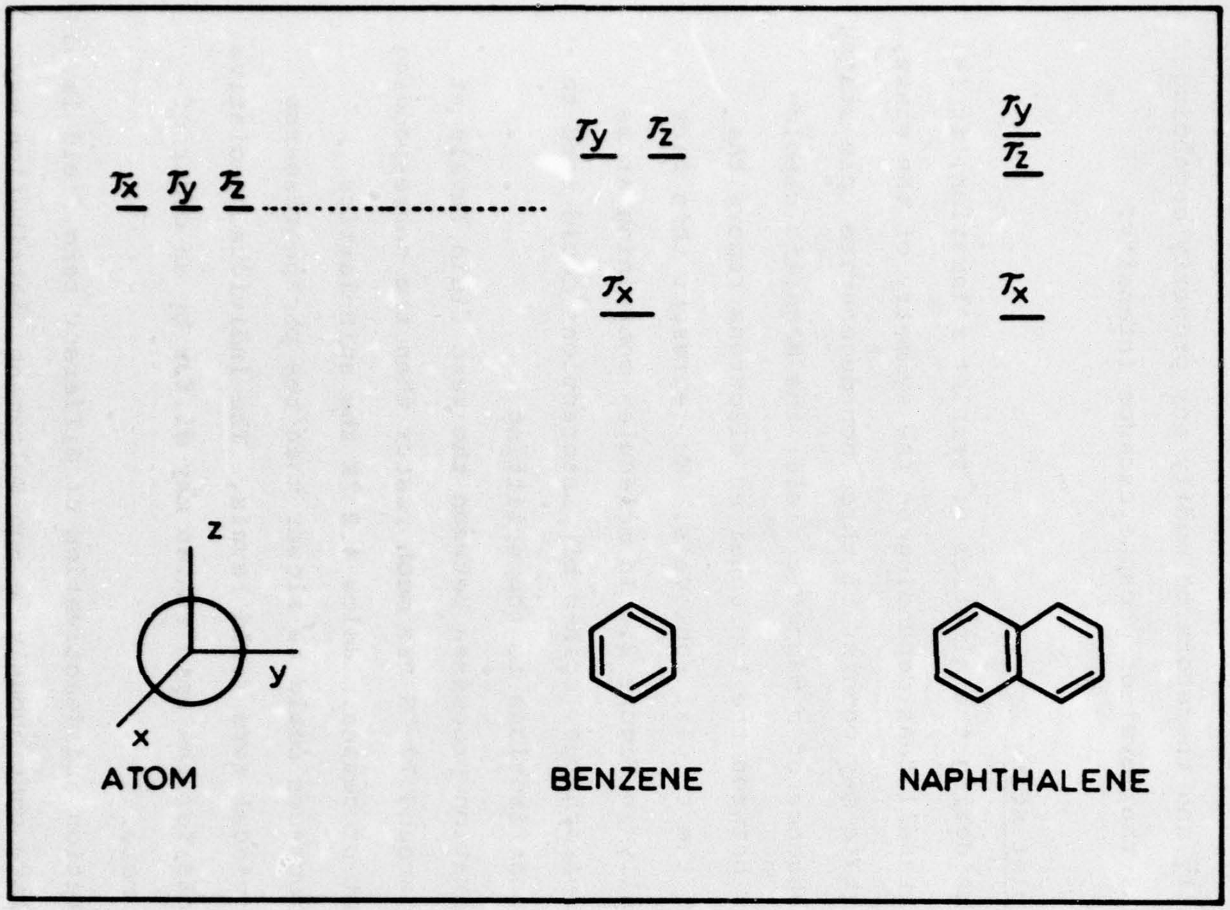

Figure 2 Zero Field Splitting in the Triplet State of Symmetric Aromatic Molecules

exist in the steady state population of the three components of the triplet, provided the spin-lattice relaxation processes are negligible.

Any perturbation which affects the steady state population of the three sublevels will also affect the phosphorescence emission intensity. Thus, saturating any of the zero field transitions with microwave radiation of resonance frequencies, will change the level of sample phosphorescence; such an experiment involving the optical detection of a magnetic resonance in zero field was first reported by Schmidt and Van der Waals.[10]

1.2 Spin-Lattice Relaxation

The energy exchange between a paramagnetic center and the lattice vibrations under the action of a perturbation H' is possible by various means, the most important of which are direct (one-phonon) processes and Raman (two-phonon) scattering processes. Let us denote the energy difference of any two states of a paramagnetic center by E_{mn}. The direct processes consist of an increase or decrease of the energy of the paramagnetic center by the magnitude of E_{mn} due to the destruction or creation of a single quantum of a lattice vibration (single phonon). Only those lattice oscillators whose frequencies ν satisfy the following condition may participate in these processes.

$$E_{mn} = h\nu$$

The transition probability of a paramagnetic center as a result of the direct process from level E_m to level E_n equals

$$A_{mn}^{(1)} = \frac{4\pi^2}{h^2} \rho(\nu) \; (H'_{mn})^2$$

Here $\rho(\nu)$ is the spectral density at the oscillator frequency and H'_{mn} is the matrix element of the spin-lattice interaction, averaged over the various states of the oscillators, which satisfy the condition $E_{mn} = h\nu$.

Raman phonon scattering processes consist of an increase or decrease of the energy of the paramagnetic center by the magnitude E_{mn} due to the destruction of quanta of lattice vibrations of frequency ν and the creation of quanta of frequency ν'; in addition it should be obvious that the following condition must be fulfilled:

$$E_{mn} = h\nu - h\nu'$$

For the probability of a transition under the influence of a Raman phonon scattering process, we have:

$$A_{mn}^{(2)} = \frac{4\pi^2}{h^2} \int (H'_{mn})^2 \; \rho(\nu)\rho(\nu') \; d\nu d\nu'$$

In Raman scattering processes, elastic vibrations of all frequencies participate. Therefore, in spite of the fact that Raman scattering processes are of second order, they play a dominant role in the relaxation mechanism if the temperature of the lattice is relatively high. At low temperature the direct processes play the main role.

A third two-phonon relaxation process was suggested and verified experimentally by Orbach.[11] It is assumed that the paramagnetic center has a set of energy levels where there are two low lying states (a), (b) and an excited state (c) whose energy is less than the maximum phonon energy. It is then possible for a paramagnetic center in state (b) to absorb a phonon of the appropriate frequency by the direct process and be excited to state (c). In this state it emits a second phonon by spontaneous or induced emission and falls down to state (a). This gives an indirect transfer of population from state (b) to state (a) and constitutes a relaxation process that may be faster than the direct transfer from (b) to (a) because of the much greater density of phonons of energy $h\nu'$. The following expression is obtained for the relaxation time:

$$\frac{1}{\tau} = \frac{24\pi^3}{h^4 \rho c_s^5} (H')^2 (h\nu')^3 \frac{1}{\exp\left\{(h\nu')/(kT_o)\right\} - 1}$$

That is in the limit where $h\nu' >> kT_o$, $1/\tau$ varies as

$$(h\nu')^3 \exp\left\{(-h\nu')/(kT_o)\right\}$$

Here ρ is the crystal density; c_s is the speed of sound in the medium; H' is a product of matrix elements between the states (a), (b) and (c); T_o is the crystal temperature.

The nature of the coupling between the electron spin moment and phonons has been investigated by several workers. In the theory of paramagnetic relaxation given by Waller[12] it was assumed that the reorientation of the spin of an atom with respect to an external magnetic field, occurs under the influence of lattice vibrations as a result of a change in the magnetic interactions of the spins caused by these vibrations. Waller's calculations led, however, to values of the relaxation time which are several orders of magnitude greater than those obtained experimentally. This mechanism seems to be important in substances with large magnetic moments of atoms and with a large density of magnetic particles where exchange forces acquire an appreciable magnitude.

Kronig[13] proposed the following reaction mechanism. The elastic vibrations modulate the electric field of the crystal which in turn changes the orbital motion of the electrons of the paramagnetic centers; through the orbital magnetic moment, the electric field of the crystal in turn acts on the electron spin. This mechanism was further elaborated by Van Vleck.[14] In general for a small number of defects, and with sufficiently strong dilution by diamagnetic particles, the Kronig-Van Vleck relaxation mechanism will predominate.

1.3 Phonon Induced Transitions

We note in the preceding discussion a similarity between the transitions induced by a microwave radiation field and those transitions caused by the interaction of the spin system with the lattice phonons. In the first instance there is coupling between the spin system and the radiation field; in the second instance there is coupling between the spin system and the lattice phonon field.

Employing piezoelectric transducers, we demonstrate in what follows a technique of optical detection that is suitable for the study of a number of processes involving photoexcited metastable states of organic molecules in the solid state. These processes include, but are not limited to, spin-phonon interaction and defect-phonon interaction.

2. EXPERIMENTAL ASPECTS

2.1 Samples Preparation

Mixed crystals of durene containing TCB were also prepared. The chemical purity of the base material was assured by extensive zone refining of Eastman reagent grade starting material. The purified durene was additively contaminated with known amounts of TCB. The mixed chemicals were completely outgassed and sealed in evacuated pyrex tubes. Crystals, approximately 3 cm long by 1 cm in diameter, were prepared by lowering the sealed tubes through a vertical Bridgman furnace arrangement over a period of 48 hours. A total of twelve samples were obtained in this manner; four were doped with 0.25% (w/w) TCB, four with 1% TCB and the remaining four with 2.5% TCB. Subsequent to the initial preparatory stages described above, the samples were divided into four equivalent sets. One set was used as a control and the others were respectively annealed for periods of 2, 7 and 21 days to remove to as great an extent as possible mechanical defects and strains. The annealing temperature was 73 °C; at the end of an annealing period the temperature of the annealing bath was lowered over a 24 hour period to room temperature in order to avoid introducing mechanical defects during the cooling period.

2.2 Optically Detected Interactions with Hypersonic Waves

The basic experimental arrangement is similar to that used for optically detected magnetic resonance experiments.[16] It is shown in Figure 3.

In a typical experiment a freshly cleaved face of a mixed crystal of durene doped with TCB was bonded to the hypersonic transducer with silicone grease. The transducer was affixed to a section of rigid stainless steel coaxial line Because the spins are sensitive to resonant photons as well as phonons, the transducer was mounted in such a fashion as to provide maximum shielding of the crystal from microwave leakage radiation.

This isolation was accomplished by use of a long microwave cut-off channel within the transducer mounting device[17] (see Figure 4). The channel behaves as a wave guide beyond cut-off for the microwaves providing at least 40 db isolation. The transducer, in the form of a 1/2 inch sapphire rod with a thin ZnO piezoelectric film vapor deposited on one end,[18] is inserted into the cut-off channel. The whole assembly, rigid coax with transducer mount and sample, was suspended in a variable temperature liquid helium Dewar, Janis Research Co., model 10DT with optical tail. The liquid helium Dewar enabled us to perform

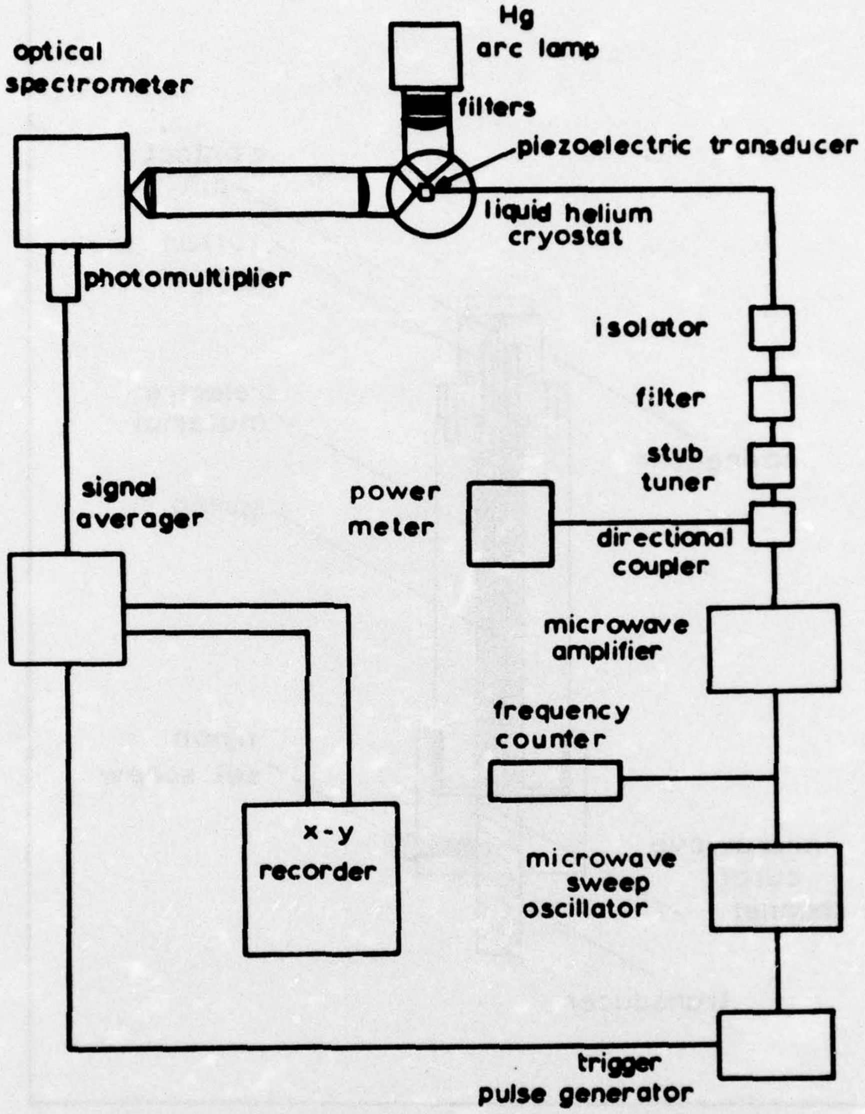

Figure 3 Experimental Arrangement for Optically Detected Interactions with Coherent Acoustic Waves

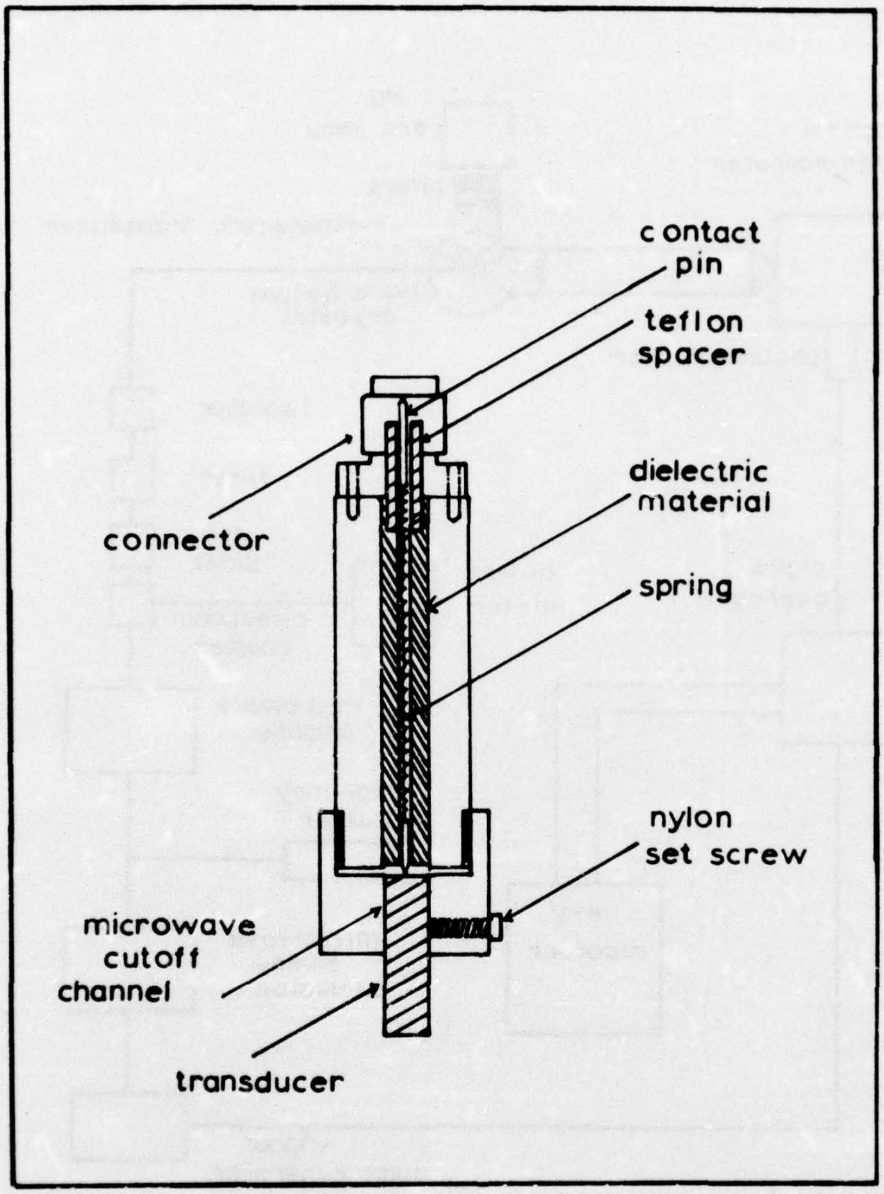

Figure 4 Piezoelectric Transducer Holder Assembly

experiments in helium vapor. By varying the pumping rate and the helium flow rate in the sample chamber, it was possible to adjust the temperature continuously from 1.4 °K to 4.2 °K in liquid helium and from 1.8 °K to 60 °K in helium vapor.

The light from a high pressure 100 W mercury short arc lamp was collimated and filtered by passage through 5 cm of an aqueous solution of $CoSO_4 \cdot 7H_2O$ (84 g/l) and $NiSO_4 \cdot 6H_2O$ (276 g/l) plus a Corning 7-54 filter to obtain the desired excitation band.

The phosphorescence was collected at a 90° angle to the exciting source, focussed through an appropriate set of quartz lenses, and dispersed by a Jarrel-Ash 1 m Czerny-Turner spectrometer equipped with a refrigerated EMI 9558 QB photomultiplier. The cathode of the photomultiplier was held at a negative potential of 1150 Volt by a Jarrel-Ash combination power supply-electrometer, model 26-780, while the output of the photomultiplier was connected to a Northern 575 signal averager.

The microwave source was a Hewlett-Packard sweep oscillator, model 8690B, equipped with 8690 series plug-ins to cover the appropriate frequency range. Its output was connected to a broad band 3 Watt TWT microwave amplifier whose output was then fed consecutively through a directional coupler, a bandpass filter, an isolator and finally terminated on a rigid 50 Ohm coaxial cable to which the transducer was affixed.

When the transducer is matched to the line characteristic impedance at a particular frequency, relatively low conversion losses can be obtained over a narrow bandwidth. Typically 5 - 7 db conversion losses could be realized within a band width of approximately 100 MHz over the entire operating range of the transducer. Additionally, coupling losses due primarily to a large acoustic impedance mismatch between the organic sample and the sapphire rod, were estimated to be about 10 db. Some of the transducers could be operated at continuous microwave power levels as high as 3 Watts; the overall conversion efficiency results in approximately 30 mWatt of coherent acoustic power in a bandwidth of approximately 30 kHz.

The sweep oscillator and averager were both triggered by a Wavetek function generator, model 142. The stored digital signal in the averager was then recorded on a Houston, model 2000, x-y recorder. Frequency measurements were made with a Systron Donner, model 1017, transfer oscillator.

To ascertain whether the transducer was functioning properly the microwave source was pulse modulated with a PIN diode switch and the acoustic echos due to reflection at the sapphire rod-sample interface were detected. The acoustic echos are reconverted to microwave radiation pulses at the piezoelectric ZnO layer; the pulses are then returned to the TWT microwave amplifier via a circulator. The output from the amplifier is fed directly to a crystal microwave detector and displayed on an oscilloscope.

2.3 Temperature Measurements

The ambient temperature of the bath was measured with a commercially calibrated germanium 4-lead resistance thermometer from Scientific Instruments Inc., or with a resistive carbon

2-lead sensor which was calibrated against the germanium temperature sensor. The temperature monitoring devices were situated at the same height as the samples within the cryostat. By adjusting the helium flow rate into the sample chamber and the pumping rate, the temperature of the liquid or vapor phase was stabilized anywhere from 1.4 °K to 4.2 °K. Ambient temperatures above 4.2 °K were obtained by heating the liquid helium just prior to its entry into the sample chamber; at these higher temperatures the pressure in the sample chamber was maintained between 1/2 and 1 atm. Stabilization was accomplished with the use of an Artronix, model 5301, cryogenic temperature controller.

3. HYPERSONIC WAVES INDUCED TRANSITIONS

3.1 Resonant Paramagnetic Absorption of Hypersound

Resonant paramagnetic absorption of hypersound consists of the selective absorption of acoustic energy by a system of paramagnetic particles.[19] Absorption occurs when the quanta of acoustic energy become equal to the interval between the magnetic energy levels. The process is better understood if we compare it to ordinary paramagnetic resonance.[20]

We consider a macroscopic sample with particles with two different spin states a and b. We specify the number of particles in the two states as N_a and N_b respectively.

The total number of spins N is a constant, but application of a microwave field will cause N_a or N_b to change as a result of induced transitions. The change of population N_a upon application of a microwave field is:

$$\frac{dN_a}{dt} = B(n_b - N_a)$$

where B is the probability of inducing a transition between the two levels. Defining

$$\Delta n = N_a - N_b$$

we substitute

$$N_a = 1/2(N + \Delta n)$$
$$N_b = 1/2(N - \Delta n)$$

thus

$$\frac{d\Delta n}{dt} = -2B\Delta n; \; \Delta n = \Delta n(0)e^{-2Bt}$$

We note that if initially we have a population difference it will eventually disappear under the action of the induced transitions. The rate of absorption of energy, dE/dT, is:

$$\begin{aligned} \frac{dE}{dt} &= N_aBh\nu - N_bBh\nu \\ &= h\nu B\Delta n \end{aligned}$$

Therefore, for a net absorption of energy Δn must be non-zero. The resonant absorption of energy would eventually stop unless there exists a mechanism for inducing transitions between N_a and N_b to reestablish the population difference. This mechanism exists because of the coupling of the spins to the lattice.

If a non-equilibrium population difference Δn exists between the two levels, we find:

$$\frac{d\Delta n}{dt} = \frac{\Delta n_o - \Delta n}{\tau_1}$$

where Δn_o is the thermal equilibrium population difference and τ_1 is the spin lattice relaxation time.
Now combining the microwave induced process and the relaxation process we get:

$$\frac{d\Delta n}{dt} = -2B\Delta n + \frac{\Delta n_o - \Delta n}{\tau_1}$$

in the steady state

$$\frac{d\Delta n}{dt} = 0$$

thus

$$\Delta n = \frac{\Delta n_o}{1 + 2B\tau_1}$$

the rate of energy absorption is:

$$\frac{dE}{dt} = \Delta nh\nu B = \Delta n_o h\nu \frac{B}{1 + 2B\tau_1}$$

this equation tells us that we can increase the power absorbed by the paramagnetic centers by increasing the intensity of the microwave field as long as

$$2B\tau_1 \ll 1$$

However, once B is large enough so that $B = 1/2\tau_1$, the power absorbed levels off and a condition of saturation exists. The connection between spin lattice relaxation and acoustic resonance is made clear if we consider acoustic resonance as an inverted paramagnetic relaxation phenomenon.[21] The energy stored by the spin system after sound absorption will by virtue of relaxation processes, be transferred back to the lattice in exactly the same way as under ordinary paramagnetic resonance.

The first experimental results on the observation of acoustic magnetic resonance are due to Proctor and Tantilla,[22] who observed the effect on the spins of Cl nuclei in crystals of $NaClO_3$ following a suggestion by Al'tschuler[23] and Kastler[24] that one should be able to reverse the spin lattice relaxation process. The transition from nuclear to electron spins was made difficult by the need to generate acoustic waves of very high frequency. This problem was successfully solved in 1959 by Jacobsen, Shiren and Tucker[25] who observed electron acoustic paramagnetic resonance of Mn^{++} spins in a quartz lattice. Since this experiment several additional investigations of the interaction of acoustic waves with electron spins have been reported the results of which have provided considerable information concerning the coupling between spins and the lattice.

Initially two methods were applied for the investigation of acoustic paramagnetic resonance; one involved the measurement of the absorption coefficient and the other the measurement of the saturation factor (see Appendix). Indirect detection techniques were also developed in which the acoustic resonance is detected by its perturbation of a coupled electromagnetic transition. Optical probes exhibiting circular dichroism were used by Anderson and Sabisky in their development of a spin phonon spectrometer[26] in which they monitored the modulation of circular dichroism due to the spin phonon interaction.

All of these techniques to date have been limited to compounds exhibiting strong spin lattice coupling, (e.g. transition metals and rare earth ions in Group II and IV metal oxide lattices). The magnitude of the interaction in organic molecules is expected to be considerably less than that encountered in transition metals or rare earth ions due to the greatly reduced spin-orbit coupling. In what follows we make use of excited triplet state organic molecules for the study of spin phonon interactions by optical double resonance techniques.

3.2 Spin-Phonon Coupling in Organic Materials

We can estimate the magnitude of spin-phonon coupling in organic materials from the observed spin lattice relaxation times (τ_1) of the triplet state paramagnetic spins. For a paramagnetic spin system (e.g., the paramagnetic excited state of an impurity molecule) in thermal equilibrium with the lattice phonon bath, the direct process spin lattice relaxation time is given by:

$$\frac{1}{\tau_1} = 2B\rho(\nu)\, d\nu$$

where B is the Einstein coefficient for a phonon induced spin transition and $\rho(\nu)\, d\nu$ is the Debye phonon energy density at the resonant frequency. Thus

$$\frac{1}{\tau_1} = \frac{12h\nu^3}{c_s^3} \left(\frac{d\nu}{\exp(\frac{h\nu}{kT}) - 1} \right) B$$

where c_s, the velocity of sound in the medium, is taken here to be identical for both longitudinal and transverse polarized waves.

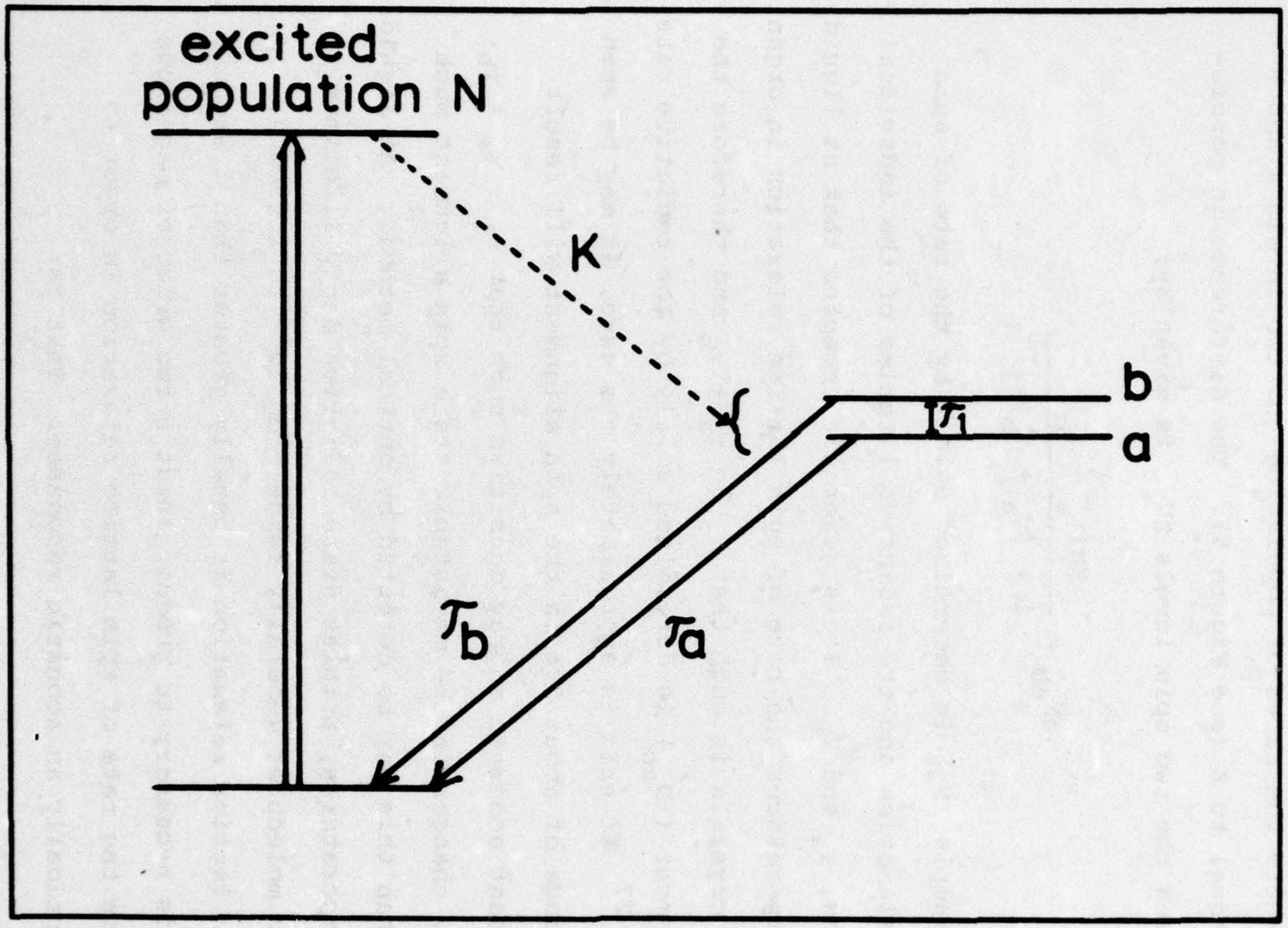

Figure 5 Energy Level Diagram for Hypothetical Two Level Photoexcited Spin System

For the purpose of illustration we consider the optical detection of acoustic resonance in a two level spin system in the case where the rates of populating the two levels a and b are each equal to K (see Figure 5). The difference in population between the two spin levels ΔN_{ab} is given by:

$$\Delta N_{ab} = \frac{KN(\tau_a - \tau_b)}{1 + (\tau_a + \tau_b)\tau_1^{-1}}$$

In this example ΔN_{ab} is determined solely by the rate of spin lattice relaxation and the radiative lifetime of the individual spin states, τ_a and τ_b. It is generally accepted that at liquid helium temperatures the rate of spin lattice relaxation in organic molecular crystals is such that $\tau_1 >> \tau_a + \tau_b$ and therefore the spin alignment (ΔN_{ab}) is determined solely by the radiative rate constants.[27] If this is approximately the case, it may be seen that a change of about 50% in the spin alignment will result with resonant acoustic energy densities such that $\tau_1 \simeq \tau_a + \tau_b$. Typically, changes in the metastable state spin alignment much smaller than this may be detected by optical methods. At liquid helium temperatures, triplet state radiative decay lifetimes of organic molecules generally range from 10^{-2} to 1 second, while spin lattice relaxation is usually greater than 1 second. Thus, it is necessary to produce about a two order of magnitude increase in the rate of spin lattice relaxation in order to observe optically an acoustic resonance. That is:

$$10^{-2} = (\tau_1)_{ac}/(\tau_1)_{th} = c_s\rho(\nu)\ \Delta\nu/P_{ac}$$

where $(\tau_1)_{ac}$ is the pumping time associated with the acoustic induced transition rate and

P_{ac} is the average acoustic power coupled into the crystal.

For $c_s = 10^5$ cm/sec, $\nu = 2$GHz, $\Delta\nu = 10^5$ Hz and T = 2 °K, we obtain P_{ac} = 4 microwatts as the power necessary for the observation of optically detected acoustic paramagnetic resonance in organic molecular crystals. Such power levels can easily be obtained from thin-film piezoelectric transducers.

3.3 Generation of Hypersound

The general form of the transducers used in our experiments is shown in Figure 6. The end of a sapphire cylindrical rod is coated with a piezoelectric ZnO thin film sandwiched between two metal electrode films which orient the applied microwave electric field perpendicular to the transducer film. The piezoelectric stress developed at the surface of the sapphire rod gives rise to a displacement which propagates in the form of a hypersonic wave inside the sapphire rod.

A hypersonic field of special interest will be formed inside the sapphire rod when the generated plane waves with incidence normal to the other face of the rod (the interface between the sapphire rod and the sample) are reflected and interfere with the incident waves following.[28] We distinguish two cases:

First Case. The waves propagate down the sapphire rod and are perfectly reflected at the interface by the sample crystal. We assume that the two media have very different acoustic impedences, $\rho_1 c_1 >> \rho_2 c_2$. At the interface for the resulting wave we find:

$$A = a_1 \cos(\omega t - kx) + a_2 \cos(\omega t + kx)$$

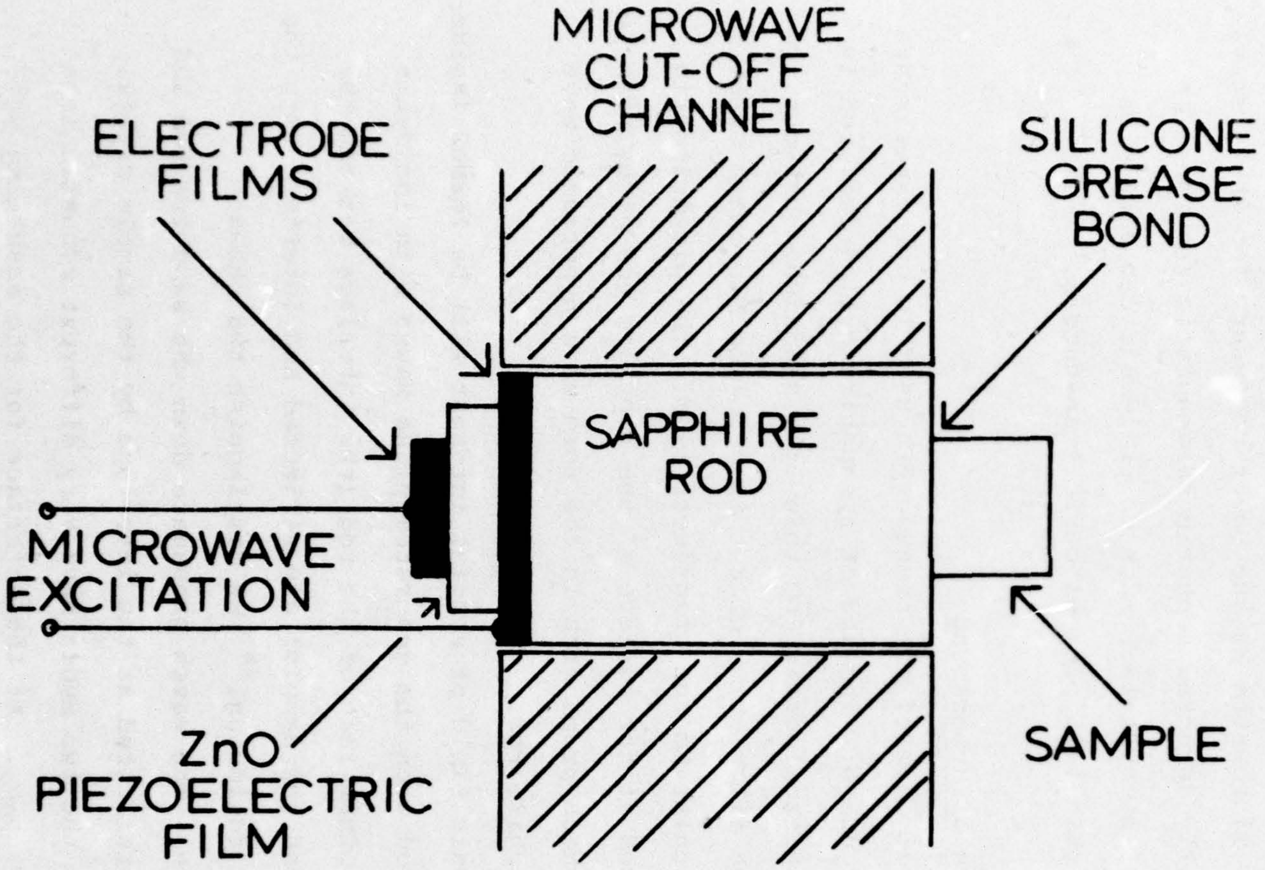

Figure 6 Piezoelectric Transducer Assembly

where A is the resulting amplitude and a_1 and a_2 are the vibration amplitudes of the incident wave and reflected wave respectively.

As the reflection is perfect and as we assume there is no energy dissipation, we have $a_1 = a_2 = a$ and hence:

$$A = 2a\cos(\omega t)\cos(kx)$$

This is the equation of a standing wave with amplitude 2a at the positions $x = 0, \lambda/2, \lambda, 3\lambda/2, \ldots$ and with zero amplitude at $x = \lambda/4, 3\lambda/4, 5\lambda/4, \ldots$ where λ is the wavelength.

Second Case. If the characteristic acoustic impedances of the two media are not very different, part of the incident energy is transmitted into the other medium at the interface and the hypothesis of perfect reflection does not apply. Thus we have $a_1 > a_2$. The displacement equation becomes:

$$A = (a_1 + a_2)\sin(\omega t)\sin(kx) + (a_1 - a_2)\cos(\omega t)\cos(kx)$$

The system can now be regarded as composed of two standing waves, one of amplitude $(a_1 + a_2)$ as if the wave were reflected by a rigid interface, and the other of amplitude $(a_1 - a_2)$ as if the wave were reflected by a compliant interface.

The nodes and antinodes of the two standing waves do not coincide but are displaced respectively by $\lambda/4$; moreover, in the resulting system there are no amplitude nodes but there will be minima of $(a_1 - a_2)$ and maxima of $(a_1 + a_2)$. This phenomenon is of great value to us for it allows us to unambiguously differ-

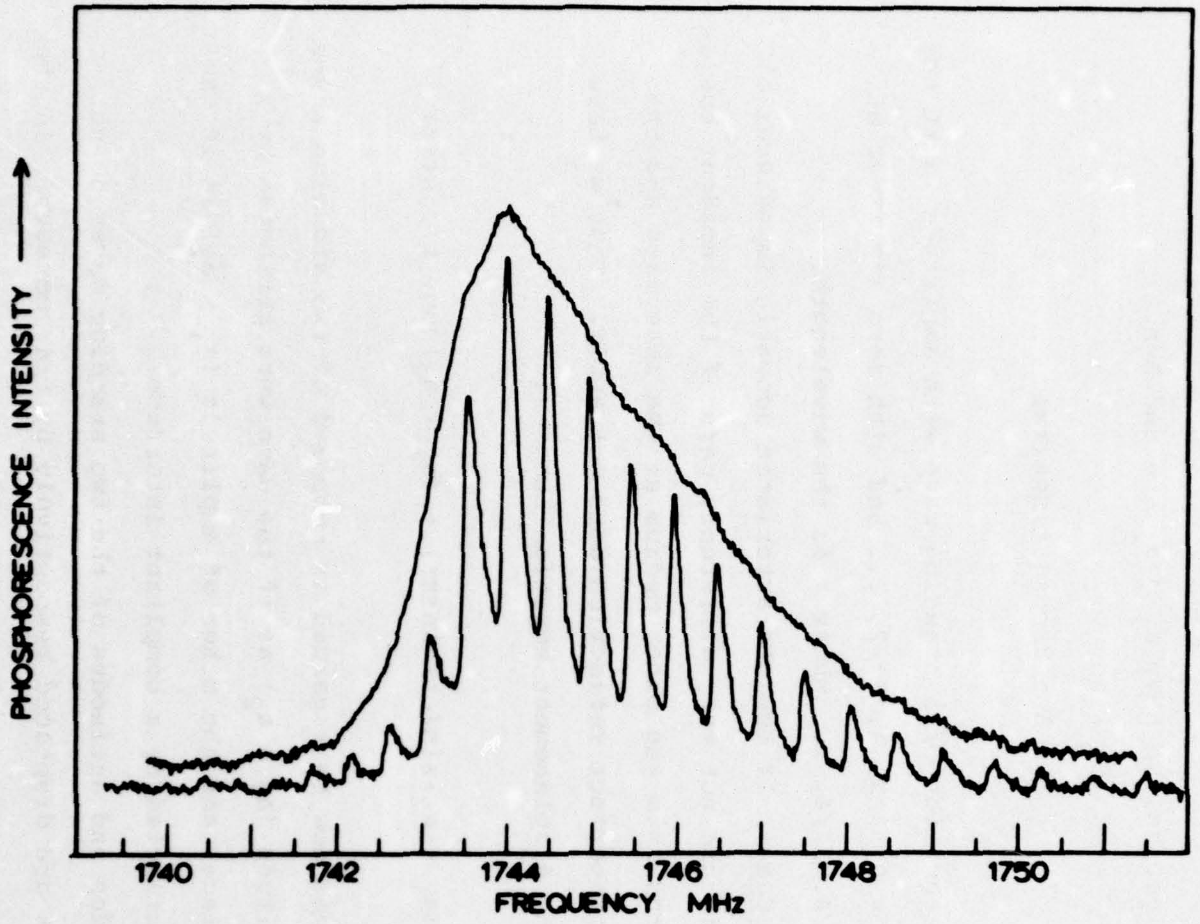

Figure 7 The 2E Optically Detected Microwave and Acoustic Resonance Spectra of TCB in Durene Obtained by Monitoring the Phosphorescence Intensity at 3782 Å

entiate an acoustic resonance from an electromagnetic field induced transition.

3.4 Optically Detected Acoustic Resonance in 1,2,4,5-Tetrachlorobenzene

In a typical experiment, a freshly cleaved (001) face of a doped durene single crystal was bonded to the ultrasonic transducer with silicone grease. The optically detected acoustic paramagnetic resonance (ODAR) spectrum obtained by sweeping the acoustic frequency in the region of the 2E and D - E transitions of TCB in durene while monitoring the phosphorescence intensity at 3782 Å is shown in Figs. 7 and 8. The multiple minima within the acoustic resonance linewidth result from standing waves within the sapphire rod. When the length of the rod corresponds to an integral number of acoustic half wavelengths, standing waves are set up within the sapphire rod and a minimum of energy is transmitted through the end of the transducer to the sample crystal. The frequency separation between successive minima is given approximately by:

$$\Delta\nu = c_s/2L$$

which for a longitudinal wave velocity in sapphire of 1.1×10^6 cm/sec and a rod length of approximately 1.1 cm yields a frequency interval of about 0.5 MHz.

The ODAR spectrum was obtained using 10 mW of microwave power, resulting in about 100 μW of acoustic power coupled into the sample. As is shown in Figure 7, the ODAR envelope is essen-

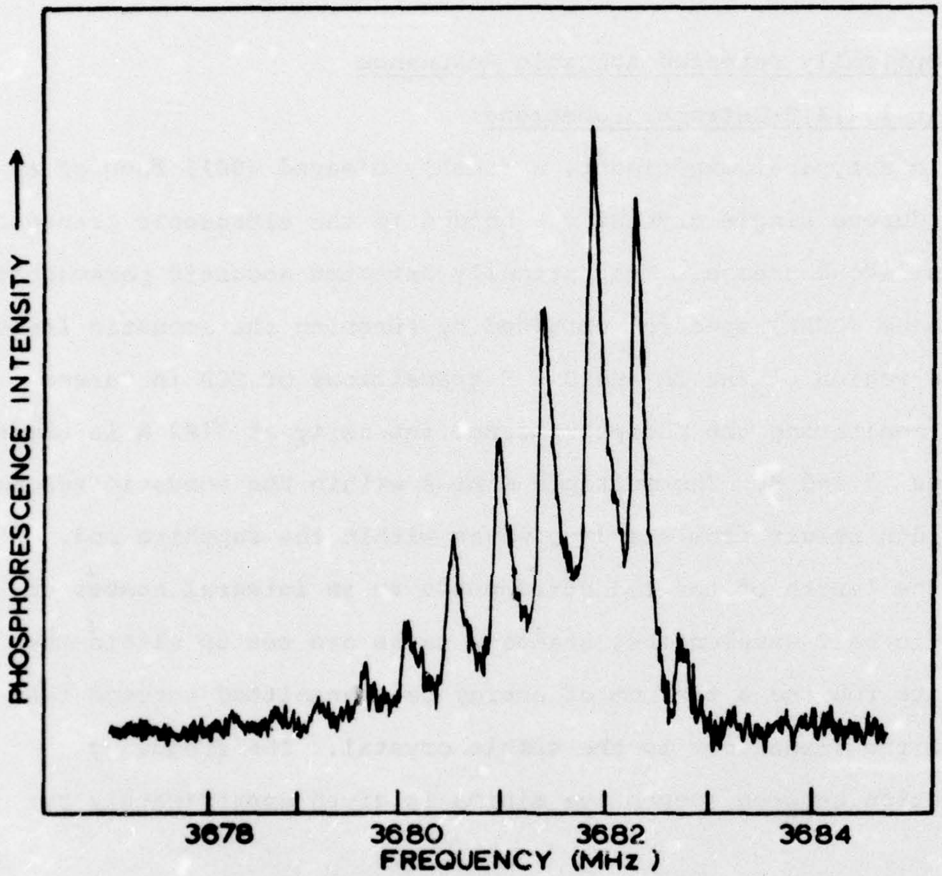

Figure 8 The D - E Optically Detected Acoustic Resonance Spectrum of TCB in Durene Obtained by Monitoring the Phosphorescence Intensity at 3782 Å

tially the same as the optically detected magnetic resonance line shape. The peak change in phosphorescence intensity of approximately 30% obtained with 100 μW of acoustic power is comparable to the signal level observed with equivalent levels of microwave power. We conclude that for TCB in durene the paramagnetic spins have roughly equivalent sensitivity to both microwave and acoustic excitation.

Figure 9 shows the ODAR spectrum for the 2E electron spin transition at relatively high acoustic power. The spectrum consists of a center peak flanked by three pairs of satellites separated from the main central peak by 34, 27 and 7 MHz respectively. The satellites result from nuclear quadrupole and hyperfine coupling of the chlorine nuclei in the excited triplet state; they appear as the acoustic power is increased.[29] The outer two pairs of satellites correspond to a simultaneous electron-nuclear transition associated with the ^{37}Cl and the ^{35}Cl isotopes. The inner pair of satellites also corresponds to simultaneous neclear and electron spin transitions, but associated with molecules that contain both isotopes. The frequency separation between these latter satellites and the central peak is simply the difference between the ^{35}Cl and the ^{37}Cl nuclear quadrupole coupling constants which are, in zero order, the separations between the outer pairs of satellites and the central peak. The interpretation is analogous to that given to observed microwave-optical double resonance spectra.

3.5 Two-Phonon Transitions

Figures 10 and 11 show results obtained by exciting the crystal at half the resonance frequencies for the D - E and the

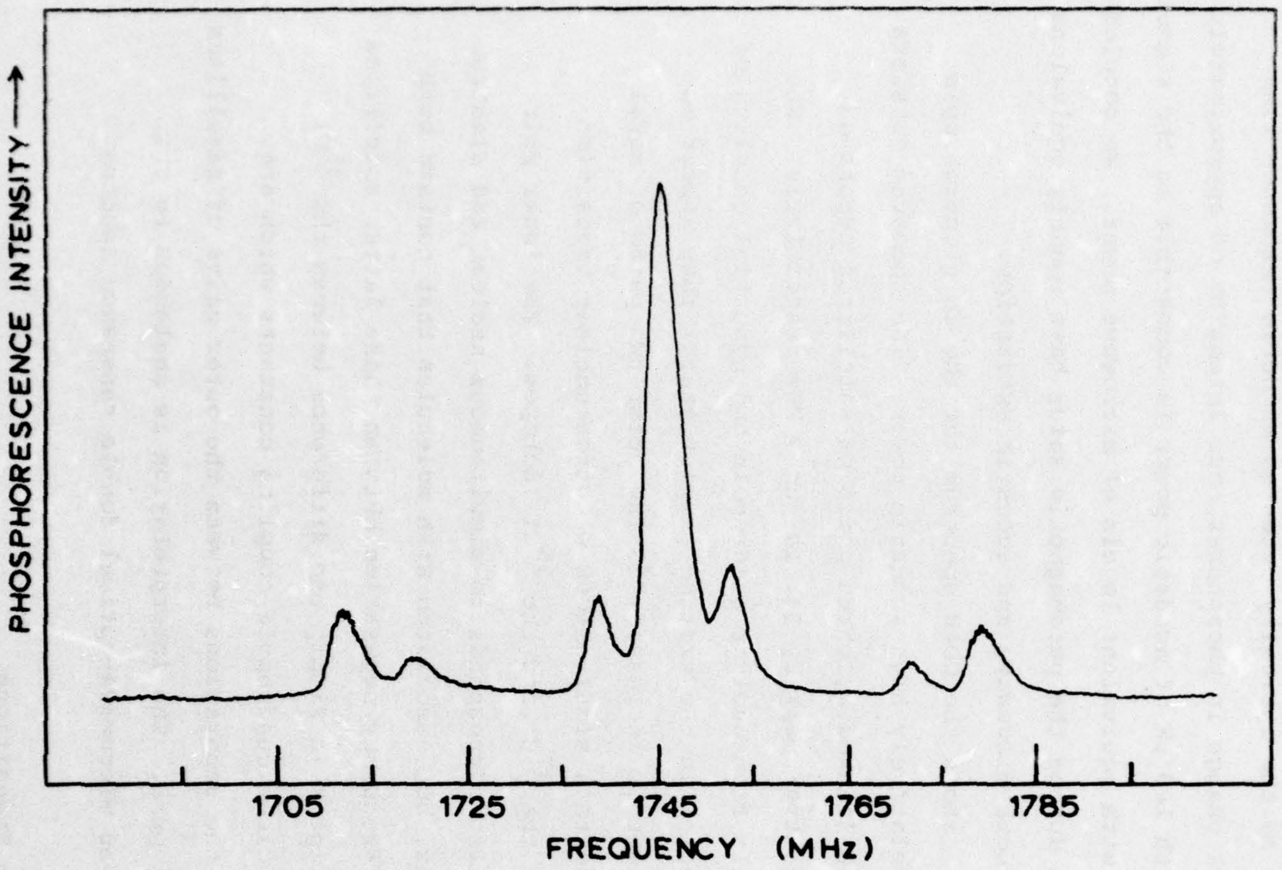

Figure 9 The 2E Zero Field Optically Detected Acoustic Resonance Spectrum of TCB in Durene Showing Quadrupole and Hyperfine Coupling of the Chlorine Nuclei in the Excited Triplet State

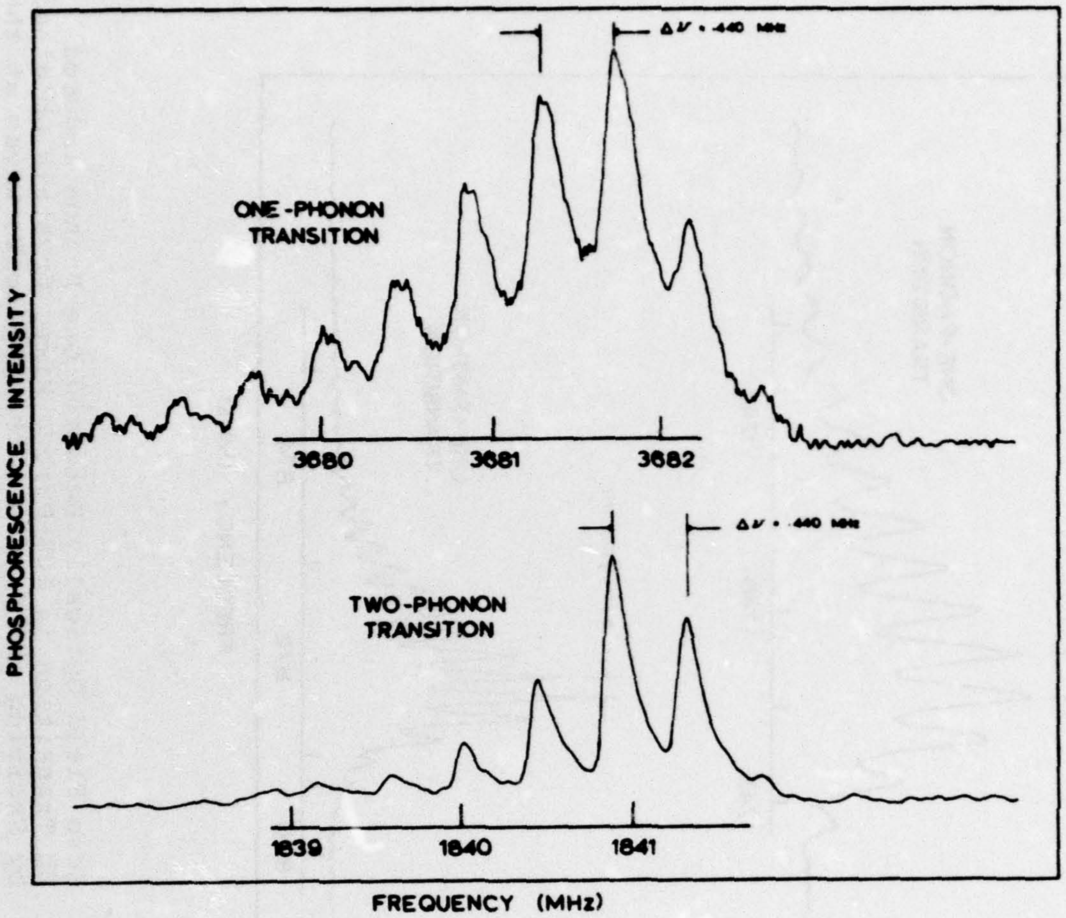

Figure 10 Zero Field Optically Detected One-Phonon and Two-Phonon Induced D - E Transition in TCB-Durene Mixed Crystals

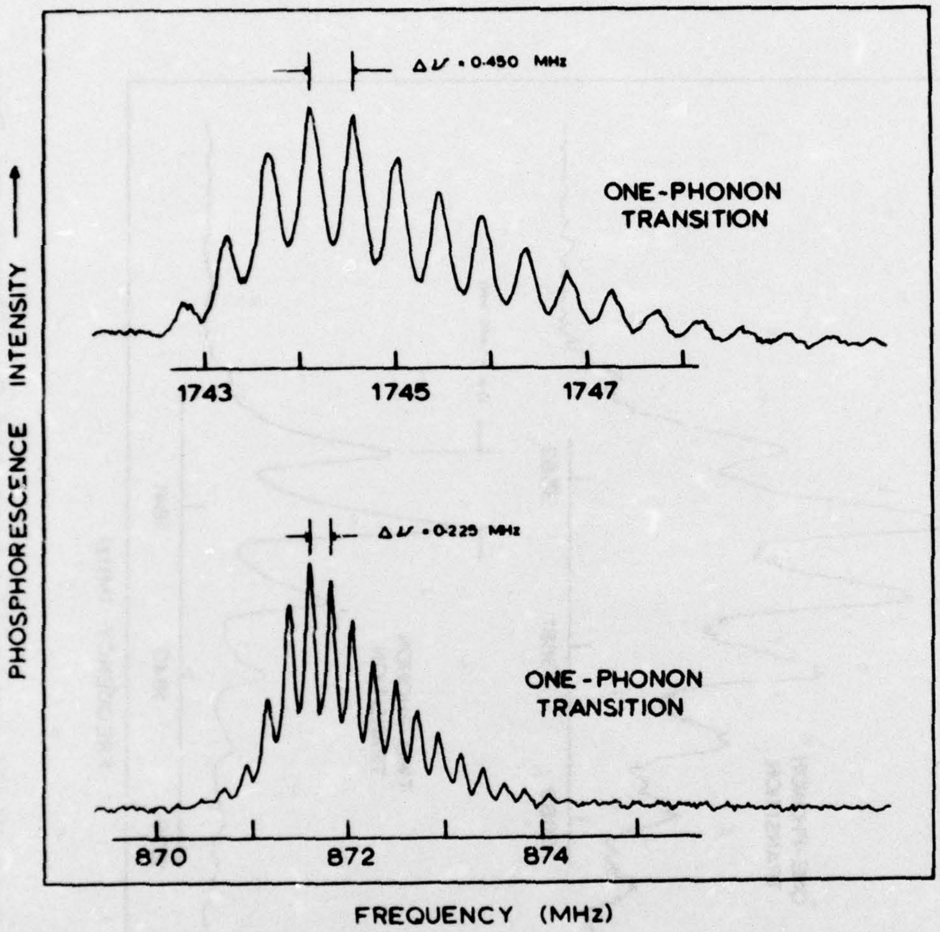

Figure 11 Zero Field Optically Detected One-Phonon Induced 2E Transition in *TCB-Durene Mixed Crystals* Obtained by Exciting the Sample with Hypersonic Waves at the Resonance Frequency and at Half the Resonance Frequency.

2E transitions. Again we observe multiple minima and maxima within the acoustic resonance linewidth resulting from standing waves within the sapphire rod. If we assume resonance to be caused by 2nd harmonics generated by the transducer we would expect a frequency response consisting of a sharp line spectrum characteristic of a resonant standing wave pattern and exhibiting a separation between successive minima equal to half the separation between successive minima in the resonance line at the fundamental frequency. The bandwidth should be half the resonance line bandwidth. If we assume a two-phonon process we would also expect a bandwidth equal to half the resonance line bandwidth, but we would expect a separation between minima in the standing wave pattern equal to the separation in the resonance line. The separation between minima is determined in the last case solely by the velocity of sound and the length of the microwave-acoustic transducer. In the first case the separation between minima would appear to be half that in the resonance line simply as an artifact for we are in effect scanning through the resonance line twice as fast. We observe both types of spectra indicating that 2nd harmonics are generated and that a reasonable effect induced by a two-phonon process does occur. The fact that we did not observe a two-phonon transition at 870 MHz does not contradict the results observed at 1841 MHz; as, the microwave-acoustic transducer is highly inefficient below 2 GHz; and the coefficient of sound absorption by the paramagnetic centers is proportional to the square of the frequency (see Appendix).

3.6 Phonon-Phonon Interaction

The experimental situation is simply that hypersonic waves interact in a crystalline solid with thermal or lattice vibration stress waves despite the fact that no such interaction should occur, even at equal frequencies, if the waves were linearly elastic.[30] With anharmonic lattice forces, however, phonons may scatter other phonons as third or higher elastic constants are involved.

Two distinct theoretical approaches have so far been used in attempting to calculate the attenuation and velocity of sound waves interacting with thermal phonons.[31]

Landau and Rumer regarded the sound wave as a beam of low energy phonons and calculated the attenuation by finding the rate at which these phonons were scattered by collisions with thermal phonons; they considered only three-phonon collisions involving a sound wave phonon and two thermal phonons.

The other approach that has been used is the Boltzmann equation method due to Akhieser. He considered the strain of the sound wave as a driving force on the system of thermal phonons, the coupling occurring because the thermal phonon frequencies depend upon the strain. As a result of this driving force, the thermal phonon system is disturbed from equilibrium, but tends to return to equilibrium because of the collisions between the thermal phonons. The character of the interaction of the hypersonic waves with thermal phonons depends on the ratio of the frequency of the hypersonic waves to the reciprocal thermal phonon relaxation time $1/\tau$. If $\omega << 1/\tau$ it is meaningless to consider individual interactions of hypersonic waves and thermal phonons since the energy of the hypersonic phonon turns out to be less than the uncertainty in the energy of the thermal phonon. Under such conditions, the elastic wave will interact with an ensemble of thermal phonons as a whole, and the elastic deformations in the hypersonic wave can be regarded as a classical field that leads to change in the frequencies of the thermal phonons. As originally developed, the theory was restricted to high temperatures where the average mean free path of the thermal phonons is much less than the wavelength of the sound wave.

For a crystal at temperature T, the average frequency ω_{av} of a thermal phonon is given by

$$h\omega_{av} = kT$$

at 10 °K $\omega_{av} = 1.31 \times 10^{12}$ sec^{-1} (approximately 200 GHz).

The highest frequency at which attenuation measurements have been reported is 114 GHz and few other measurements have been made above 10 GHz.[32] Thus it is generally true that $\omega << \omega_{av}$ where ω is the angular frequency of the monochromatic elastic wave.

If the wavelength λ of the acoustic wave is less than the mean free path ℓ of the thermal phonons, one can assume the wave to interact with individual lattice modes. This condition is generally met when one is considering the attenuation of lattice waves by other lattice waves; this condition is also met when considering hypersonic waves at very low temperatures. At low temperatures the anharmonic processes are negligible, and the attenuation of lattice waves or acoustic waves of high frequency arises from the elastic scattering of phonons by various imperfections. As the temperature is raised, anharmonic processes become increasingly important, and the additional attenuation increases rapidly with temperature.

Our experimental results are seemingly in accordance with the preceding discussion. When the crystal is immersed in helium above its lambda point or in helium vapor, it is clear that a greater impedance mismatch between the crystal and the bath exists and appreciably higher acoustic power densities may be realized than when the crystal is immersed directly in superfluid helium. As the sample is decoupled from the helium bath, sufficient inelastic scattering occurs to produce a phonon bandwidth which is large compared to the total zero field splitting. Under these conditions the ODAR spectrum consists of a broad structured band from approximately 1 - 4 GHz corresponding to an increase in phosphorescence intensity.

Figure 12 shows the results of a temperature variation study. Rapidly as the temperature is increased inelastic scattering of phonons into the bandwidth of the spins becomes dominant; this is clearly shown by the broadening of the optically detected acoustic resonance line. We conclude that first order relaxation processes become insignificant as the temperature is raised above 4 °K.

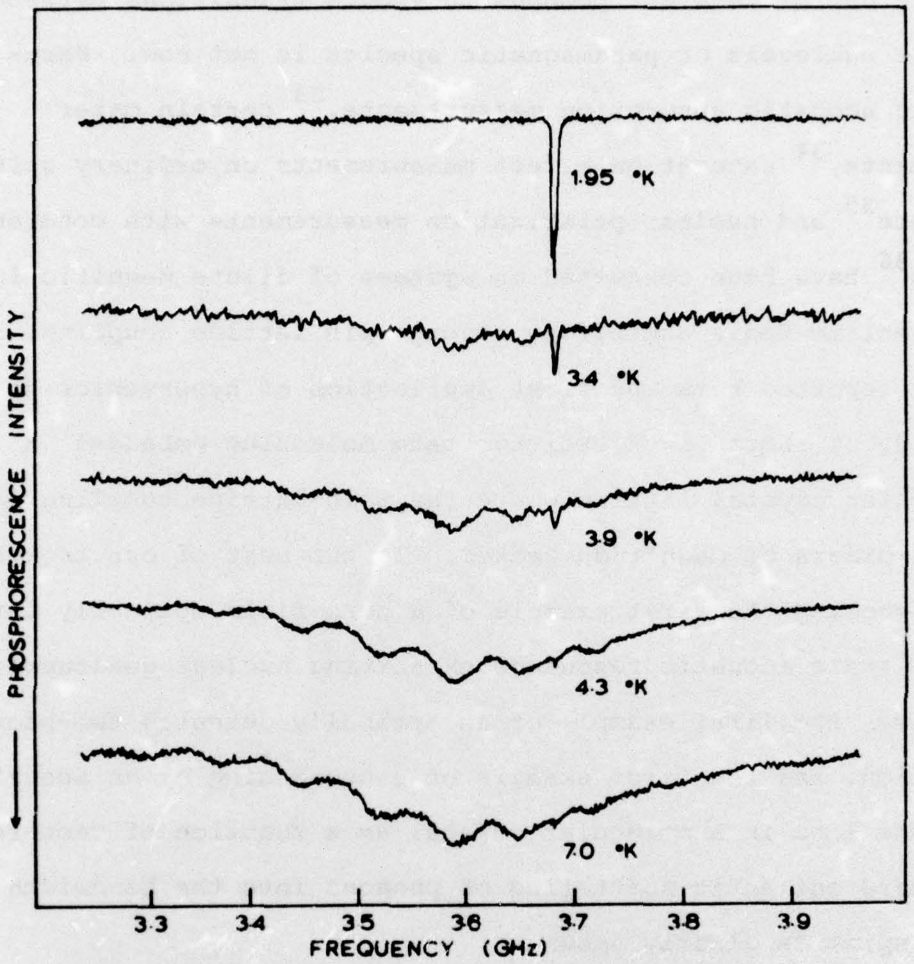

Figure 12 Inelastic Scattering of Coherent Phonons as a Function of Temperature, Detected via Spin-Phonon Coupling in the TCB-Durene Mixed Crystal System

4. CONCLUSION

The use of coherent phonons to induce transitions between magnetic sublevels of paramagnetic species is not new. Paramagnetic acoustic absorption measurements,[33] certain maser experiments,[34] saturation effect measurements on ordinary spin resonance[35] and nuclear polarization measurements with coherent phonons[36] have been conducted on systems of dilute magnetic ions in dielectric media exhibiting strong spin lattice coupling. We have reported here the first application of hypersonics to the study of short lived excited state molecules embedded in a molecular crystal lattice where the spin lattice coupling is several orders of magnitude weaker. To the best of our knowledge we are showing the first example of a zero field optically detected excited state acoustic resonance exhibiting nuclear quadrupole structure, the first example of an optically detected two-phonon transition, and the first example of a broadening of an acoustic resonance line in a molecular crystal as a function of temperature where inelastic scattering of phonons into the bandwidth of the spins is clearly shown.

The extension of the method described to other systems and for different purposes is quite evident, the limitation at the present time being the frequency limit on hypersonic waves which can be conveniently generated. In what follows we point out a number of possible applications.

4.1 Spin Coherent-Phonon Interaction

The paramagnetic absorption of coherent phonons in molecular crystals can, in principle, give information which is difficult to obtain by conventional EPR measurements. For example the study of the spatial anisotropy in spin lattice coupling and of the differences in coupling involving longitudinally and transverse polarized phonons seems quite possible. Direct investigation of spin-phonon interaction, usually deduced from spin lattice relaxation times (τ_1), can be carried out. The dependence of the spin phonon interaction on factors such as defect and spin concentration may be determined; in this regard, the use of isotopic mixed crystals would permit the study of the effect of the concentration of the spins over a wide range and would limit the introduction of mechanical defects.

4.2 Development of a Hypersonic Waves Generator

It was pointed out by Van Vleck[37] and later by Kastler[24] that spin lattice relaxation by the direct process creates acoustic waves with a well defined frequency. If the lattice thermal relaxation time τ_L is greater than the spin lattice relaxation time τ_1 a phonon "bottleneck" situation will exist. Thus magnetic resonance may constitute a technique of generating hypersonic waves of narrow band. It might be possible to detect such hypersonic waves with highly sensitive and selective thin film heat sensors. Preliminary results in our laboratory indicate that such sensors are quite easy to construct and highly sensitive.

APPENDIX

Measurement of the Absorption Coefficient and of the Saturation Factor in Acoustic Paramagnetic Resonance[38]

The probability per second that a paramagnetic center undergoes a transition between magnetic levels a and b, absorbing one quantum of lattice vibration, is equal to:

$$A_{ab} = \frac{2^{\pi}}{h^{2}} \rho(\omega) \quad (a,n_{\omega}/H_{s-p}/b,n_{\omega} - 1)^{2}$$

where $(a,n/H_{s-p}/b,n - 1)$ is the matrix element of the Hamiltonian for the spin phonon interaction; n_{ω} is the number of phonons with the resonance frequency ω; and $\rho(\omega) = \frac{\omega^{2}V}{2^{\pi 2}}$ is the spectral density of longitudinal or transverse plane polarized phonons propagating in a crystal of volume V with velocity c_s. Assuming nearly monochromatic sound vibrations with a bandwidth equal to $\Delta\omega$, the incident energy passing per second through unit area is:

$$E_i = c_s \, \rho(\omega) \, n_{\omega} h\omega(\Delta w/V)$$

Assuming $\Delta\omega <<$ (the line width of the resonance), the energy of the sound waves absorbed per second per unit volume at temperature T is:

$$E = NA_{ab} \frac{(h\omega)^{2}}{kT} g(\omega)\Delta\omega$$

where $\int g(\omega)\, d\omega = 1$ and $g(\omega)$ gives the shape of the absorption line.

A coefficient of sound absorption is obtained as follows:

$$S_{ab} = \frac{E}{E_i} = \frac{2^{\pi}}{h^2} \frac{Nh\omega V}{kTc_s n_\omega} g(\omega) \ (a, n_\omega / H_{s=p} / b, n_\omega - 1)^2$$

The form of H_{s-p} is complex and has been derived for crystals containing transition metal ions and assuming the main role in the spin phonon interaction is played by the Kronig-Van Vleck mechanism. Some general conclusions can be stated. Firstly, to a high degree of accuracy the matrix elements do not depend on the frequency and therefore the coefficient of sound absorption, S_{ab}, is proportional to ω^2. Secondly, the coefficient S_{ab} is inversely proportional to the temperature T of the crystal if the occupation of the levels a and b has the same dependence on T. Of course, in our experiment, the difference in occupation of levels a and b is produced as a result of the anisotropy of the spin orbit interaction; we do not necessarily have a Boltzmann population distribution. Finally, the velocity of propagation of sound is very important as S_{ab} is proportional to $1/c_s^3$. Thus absorption of transverse and longitudinal waves will be very different.

Measurement of the absorption coefficient gives direct information concerning the spin phonon interaction. But the application of this method requires absolute measurements of the loss of acoustic power resulting both from the resonance effect as well as from other causes; this is difficult.

In the method of saturating the paramagnetic resonance which is widely used for measuring spin lattice relaxation times, one uses the following formula for the saturation factor q_{ab}. Assuming a spin 1/2 system we have:

$$q_{ab} = \frac{N_a - N_b}{N_a^o - N_b^o} = (1 + 2\tau_{ab}B_{ab})^{-1}$$

where $N_a^o - N_b^o$ is the difference in population at equilibrium and $N_a - N_b$ is the difference under saturation conditions; B_{ab} is the probability of transition under the influence of an acoustic field, and τ_{ab} is the relaxation time.

References

1. M. J. Buckley, A. H. Francis, Chem. Phys. Lett., 23, 582 (1973).

2. Photochemistry, Ed. D. Bryce-Smith, Stonebridge Press, Bristol, G.B., p. 43 (1975).

3. F. Bitter, Phys. Rev., 76, 833 (1949).

4. J. Brossel and A. Kastler, Compt. Rend., 229, 1213 (1949).

5. J. Brossel and F. Bitter, Phys. Rev., 86, 308 (1952).

6. A. Kastler, Physics Today, 20, 34 (1967).

7. S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Lett., 3, 545 (1959).

8. M. Sharnoff, J. Chem. Phys., 46, 3263 (1967).

9. A. L. Kwiram, Chem. Phys. Lett., 1, 272 (1967).

10. J. Schmidt and J. H. van der Waals, Chem. Phys. Lett., 2, 640 (1968).

11. C. B. P. Finn, R. Orbach and W. P. Wolf, Proc. Phys. Soc. (London), 77, 261 (1961).

12. J. Waller, Z. Physik, 79, 370 (1932).

13. R. L. Kronig, Physica, 6, 33 (1939).

14. J. H. Van Vleck, Phys. Rev., 57, 426 (1952).

15. G. A. George and G. C. Morris, Mol. Cryst. Liq. Cryst., 11, 61 (1970).

16. M. J. Buckley and C. B. Harris, J. Chem. Phys., 56, 137 (1972).

17. C. H. Anderson and E. S. Sabisky, in: "Physical Acoustics" (W. P. Mason and R. N. Thurston, eds.), Vol. VIII, p. 29, Academic Press, New York, (1971).

18. J. de Klerk, in: "Physical Acoustics" (W. P. Mason, ed.), Vol. IV, p. 195, Academic Press, New York, (1966).

19. E. B. Tucker, in: "Physical Acoustics" (W. P. Mason, ed.), Vol. IV, p. 47, Academic Press, New York, (1966).

20. C. P. Slichter, "Principles of Magnetic Resonance," p. 4, Harper & Row, New York, (1963).

21. S. A. Al'tshuler and B. M. Kozyrev, "Electron Paramagnetic Resonance," Academic Press, New York, (1964).

22. W. G. Proctor and W. H. Tantilla, *Phys. Rev.*, **101**, 1757 (1956).

23. S. A. Al'tshuler, *Sov. Phys. JETP*, **1**, 37 (1955).

24. A. Kastler, *Experientia*, **8**, 1 (1952).

25. L. H. Jacobsen, N. S. Shiren and E. B. Tucker, *Phys. Rev. Lett.*, **3**, 81 (1959).

26. C. H. Anderson and E. S. Sabisky, *Phys. Rev. Lett.*, **18**, 236 (1967).

27. S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

28. A. Barone, in: "Encyclopedia of Physics" (S. Flugge, ed.), Vol. 11, pt. 2, p. 74, Springer Verlag, Berlin, (1962).

29. D. S. Tinti, M. A. El-Sayed, A. H. Maki and C. B. Harris, *Chem. Phys. Lett.*, **3**, 343 (1969).

30. P. G. Klemens, in: "Physical Acoustics" (W. P. Mason, ed), Vol. III, p. 201, Academic Press, New York, (1965).

31. H. J. Maris, in: "Physical Acoustics" (W. P. Mason, and R. N. Thurston, eds.), Vol. VIII, p. 279, Academic Press, New York, (1971).

32. J. Ilukor and E. H. Jacobsen, *Science*, **153**, 1113 (1966).

33. E. B. Tucker, *Phys. Rev. Lett.*, **6**, 183 (1961).

34. E. B. Tucker, *Phys. Rev. Lett.*, **6**, 547 (1961).

35. N. S. Shiren and E. B. Tucker, *Phys. Rev. Lett.*, **6**, 105 (1961).

36. C. B. Jeffries, *Progr. Cryog.*, **3**, 149 (1961).

37. J. H. Van Vleck, *Phys. Rev.*, **59**, 724 (1941).

38. S. A. Al'tshuler, B. I. Kochelaev and A. M. Leushin, *Soviet Phys. USP.*, **4**, 880 (1962).

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