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DISCLAIMER

Magnetic resonance spectrometer with a dc SQUID detector

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ABSTRACT

We describe a dc SQUID (Superconducting QUantum Interference Device) based magnetic resonance spectrometer particularly suited to measurements in the frequency range of 100 kHz to several megahertz. Results are presented for NQR (Nuclear Quadrupole Resonance) of boron-11 in boron nitride at 4.2 K, yielding ω_Q = 1467 ± 2 kHz. We also present a direct measurement of the methyl group tunneling frequency, ω_t = 210 ± 10 kHz, of propionic acid in low field, at 4.2 K.

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INTRODUCTION

Many quadrupolar nuclei have NQR (nuclear quadrupole resonance) splittings in the range from 100 kHz to several megahertz, among them boron-11, oxygen-17, and aluminum-27. Measurements of quadrupolar splittings in this range are difficult to carry out either in high magnetic field, or in zero field. In high field, the distribution of transition frequencies, caused by random orientations of the crystal axes with respect to the magnetic field, results in excessive broadening and a loss of direct information about the quadrupolar splitting.[1] In zero field, the low transition frequencies result in poor signal-to-noise ratios for conventional spectrometers, which use a detection system based on Faraday's Law. For these detectors, the voltage induced in a coil around the sample is proportional to the rate of change of the magnetization. The measured signal amplitude is therefore strongly dependent on the transition frequency.

We have constructed a magnetic resonance spectrometer which uses a dc SQUID (Superconducting QUantum Interference Device)[2] to detect the magnetization of a spin system as a function of the frequency of an applied rf (radio frequency) field.[3,4] Since the SQUID can measure magnetic flux directly, rather than the time-derivative of the flux, it is not subject to the frequency dependence of Faraday Law detectors. The SQUID measures the dc component of the sample magnetization, so for a given sample magnetization, the sensitivity of the experiment is almost independent of the frequency of the transition. Thus we are able to directly measure low frequency NQR transitions with high sensitivity. In addition, we are able to explore transitions in spin-1/2 systems that are normally forbidden in high field. For example, spin eigenstates of a tunneling methyl group can be characterized as having either A or E symmetry.[5] The interaction of an rf field with a nuclear spin in high field has A symmetry, so transitions between states of different symmetry cannot be induced by rf fields in high magnetic field. In low field, non-secular terms in the dipolar interaction become important, so symmetry-forbidden transitions can easily be observed, usually by field cycling.[6]

The technique involves measuring the magnetization of a sample in a small longitudinal magnetic field as a weak transverse rf field is swept through the resonance position. For quadrupolar nuclei, the quadrupolar order is transferred to Zeeman order, producing a large increase in the magnetization at the resonance frequency.[3] For spin-1/2 nuclei, the rf field saturates the spins, causing the magnetization to vanish at resonance.[4] We have previously published results on aluminum-27 using this technique.[7] In this paper we describe our spectrometer and show examples of low frequency boron-11 NQR and proton NMR (nuclear magnetic resonance) experiments.

APPARATUS

A schematic of the low-temperature part of the apparatus is shown in Fig. 1. The sample to be examined is contained in a thin-walled 5 mm diameter Pyrex NMR tube, fixed to the end of a moveable rod. This design allows the sample to be changed without removing the SQUID from the helium bath. A 10 turn pickup coil, wound of 0.13 mm diameter Formvar-insulated NbTi wire on a 6.5 mm diameter form, detects the flux generated by the sample. The leads between the pickup coil and the SQUID input terminals are shielded by a small 60/40 lead-tin tube. The pickup coil, in conjunction with a coil coupled directly to the SQUID, forms a superconducting flux transformer (Fig. 2).

The calculated inductance of the pickup coil, $L_p \sim 2\ \mu H$, matches the inductance of the coil coupled to the SQUID, L_c, to maximize the flux transfer from the pickup coil to the SQUID.[8,9] The flux through the SQUID, Φ_s, is given by

$$\Phi_s = \frac{M_{cs}}{L_p + L_c} M_a \pi r_p^2 N_p f \qquad [1]$$

where M_a is the sample magnetization, r_p is the pickup coil radius, N_p is the number of turns in the pickup coil, and f is the effective filling factor. Estimates of f must take into account not only the relative geometries and dimensions of the pickup coil and the sample, but also all superconducting materials in the vicinity of the sample.[10] Flux distortion by these materials can change the value of f by an order of magnitude or more. As an alternative to performing this calculation to estimate f, we made a direct measurement of the flux transfer, using a solenoid of approximately the same dimensions as the sample. Passing a current through the solenoid, while it is in the position the sample normally occupies, generates flux through the SQUID. By measuring the current required to change the flux through the SQUID loop by a given amount, we find that a few percent of the flux generated by the sample is coupled into the SQUID.

Radio-frequency radiation is generated in the sample by a Helmholtz saddle coil along the x-axis. Each half of the coil is 16 mm in diameter and 26 mm long, wound from 3 turns of 32 AWG (0.20 mm diameter) copper wire. A Helmholtz coil, situated along the y-axis, is used to generate circularly polarized rf by simultaneously feeding rf with the appropriate phase into each coil. The rf strength in the sample region is roughly calibrated by inserting a small coil into the sample area while the apparatus is immersed in liquid helium. Typical rf fields employed are on the order of 1 μT.

A low dc magnetic field, ranging up to about 10 mT, is provided by flux trapped in a lead tube, measuring 30 mm in diameter by 50 mm long, along the z-axis. While cooling down the apparatus, current is passed through a copper solenoid wound tightly on the outside of the lead tube. Various magnetic resonance methods were used to measure the exact value of the field when required. By passing a current through the solenoid while the lead tube is in the superconducting state, we determine that the tube attenuates external fields by a factor of about 10^6 at the pickup coil. Further attenuation is obtained by lead shielding (not shown in Fig. 1) on the inside and outside of the brass sample chamber, and by μ-metal cylinders outside the cryostat. The μ-metal also insures that the field inside the cryostat is as small as possible while cooling down the apparatus. This measure is necessary to prevent trapping flux in the SQUID shielding and other superconducting structures.

All coil forms are machined from MACOR, a mica glass-ceramic, to tolerances of a few thousandths of an inch. Vacuum grease is spread between the coil forms before assembly, providing a very rigid structure when cold. This rigidity is necessary to prevent microscopic movement of the pickup coil within the inhomogeneous dc magnetic field. Such movement can cause large changes in the flux through the pickup coil, with a corresponding large increase in the noise level in the SQUID output. This construction method has the advantage that the coil assembly can be easily dismantled, allowing modification or replacement of any particular coil. In addition, the rf coils can be rotated while warm to minimize their coupling to the pickup coil. All the coils are potted in either epoxy or cyanoacrylate glue. Although the MACOR contains several NQR and NMR active nuclei, including aluminum-27, boron-11, and fluorine-19, we do not observe any background signal in the low-field NQR experiments. Possible explanations are that the spin-lattice relaxation times of these nuclei are very long, the NQR resonances are outside the frequency range of our experiments, or there is an extremely broad range of resonance frequencies. In the NMR experiments at about 10 mT, we see a small broad background signal near the proton Larmor frequency, probably from the cyanoacrylate glue on the pickup coil. However, the sign of the background signal is opposite to that from the sample, since these protons are on the outside of the pickup coil. Thus the background signal can be easily identified, and subtracted off if necessary.

To isolate the SQUID from rf pickup, we place three small shunt resistors in parallel across the SQUID input terminals,[11] as shown in Fig. 2. This resistance, R, combined with the parallel inductance of the flux transformer, forms a low pass filter with a cutoff frequency of

$$f_o = \frac{R(L_c + L_p)}{2\pi L_c L_p} \quad . \qquad [2]$$

Each shunt resistor, made from multiple strands of manganin wire, is connected in series to a thin lead bridge. A thread connected to each bridge leads outside the cryostat. This arrangement permits removal of any resistor from the pickup circuit, while the SQUID is operating, by breaking the lead bridge. The shunt resistance is typically a fraction of an ohm, leading to a cutoff frequency of tens of kilohertz. The shunt resistor arrangement is protected from electromagnetic interference by a tight lead-lined copper shield (see Fig. 1).

A commercial dc SQUID,[12] operating in the flux-locked mode, acts as a linear flux-to-voltage converter. The SQUID housing is solidly secured to the remainder of the apparatus. The entire assembly is mounted in a stainless steel cryostat, housed in a copper mesh Faraday cage. The SQUID control unit and the remainder of the electronics are located outside the cage (see Fig. 3). The output of the SQUID control unit is passed through a low-pass filter, with a cutoff frequency from 200 Hz to 0.02 Hz and gain variable from 10 to 100. The filtered signal is digitized by a PC based data acquisition unit, then stored on the PC for further analysis.

The rf field is supplied by a Hewlett-Packard 3326A dual channel synthesizer, which operates up to 13 MHz. In two-phase mode the synthesizer generates two channels of rf with the same frequency but a constant phase difference. This feature is very useful in experiments requiring circularly polarized rf. The setup and operation of the synthesizer are controlled by the PC via the HP Interface Bus.

PERFORMANCE AND EXPERIMENTAL RESULTS

The spectrometer is currently being used to measure quadrupolar splittings in a variety of compounds. In Fig. 4 we present the boron-11 NQR spectrum of boron nitride, typical of those obtained. The spectrometer is roughly calibrated by placing a short solenoid, of about the same dimensions as the sample, into the sample chamber. The result of this calibration gives a measured magnetization of 8×10^{-6} A/m for this sample. The shoulder on the low-frequency side of the main peak, which is observed in powder samples and also in hot-pressed rods of boron nitride (both purchased from Electronic Space Products International), has not previously been reported. A discussion of the possible source of this resonance will be published separately. The position of the main peak, 1467 ± 2 kHz, is in agreement with a previous room temperature measurement, 1480 ± 50 kHz.[13]

A further application of our spectrometer is the measurement of transitions that are forbidden in high field. An example of a spectrum with such transitions, from a quantum tunneling methyl group, is shown in Fig. 5. The calculated sample magnetization, 1.4×10^{-4} A/m, compares reasonably well with the observed magnetization, 8×10^{-5} A/m. The transitions between the states of different symmetry, and the transition at twice the Larmor frequency, are not normally observable in high field NMR. The frequencies of the transitions at ω_t and $\omega_o + \omega_t$ directly give the tunnel splitting, 210 ± 10 kHz. This agrees with a measurement done by field cycling at the same temperature.[14] We expect this technique will be useful for measuring tunnel splittings in the range 100 kHz to several megahertz, a range not easily accessible by conventional NMR measurements.

The observed noise in our spectrometer, as in most SQUID based susceptometers, is dominated by noise generated by the pickup coil assembly, rather than by the intrinsic noise in the SQUID detection system.[15,16] The observed noise with a superconducting short across the SQUID input terminals is about 10^{-5} $\phi_o/\sqrt{Hz}$, where $\phi_o = 2.07 \times 10^{-15}$ Wb (1 flux quantum). The observed noise of the complete system, with low dc and rf fields, is on the order of $10^{-3}\ \phi_o/\sqrt{Hz}$. Higher rf and dc magnetic fields produce correspondingly higher noise in the total system. We expect this noise increase is due to a combination of effects, including coupling between the pickup coil and the rf coils, movement of the pickup coil with respect to the dc field, temperature fluctuations of the apparatus, and flux movement in superconductors near the pickup coil. As is usual, the noise figures refer to the equivalent flux noise through the SQUID. To calculate the equivalent flux noise through the pickup coil, which determines the minimum observable flux, these noise figures are multiplied by the number of flux quanta in the sample required to produce one flux quantum through the SQUID.

DISCUSSION

Our SQUID spectrometer, coupled with the technique of z-axis magnetization detection, presents several advantages over conventional magnetic resonance methods for certain experiments. One important advantage of the system is its extremely wide usable frequency range. Since we detect magnetization which changes very slowly, independent of the transition frequency, we are not limited by the frequency response of the SQUID feedback circuit. This feedback frequency is typically less than a few hundred kilohertz. A broad system bandwidth is important for NQR, since the splittings may vary by an order of magnitude or more within a particular compound.

Since the rate of change of the magnetization is on the order of $1/T_1$, rather than $1/T_2$, we are able to filter the output of the SQUID into a very narrow bandwidth, typically on the order of 1 Hz. The noise observed in the spectrum has a frequency distibution ranging from this filter cutoff frequency down to the inverse of the sweep time, which is usually about 100 seconds. Noise measurements on our system indicate that the observed noise is dominated by 1/f noise below about 1 Hz, so some reduction in noise level would be obtained by signal modulation.

As in conventional cw NMR, a very efficient rf filtering scheme is required if this technique is to succeed. Since we are irradiating at frequencies above the frequency response of the flux-locking circuit of the SQUID, any rf leakage into the SQUID will effectively modulate the flux-voltage curve of the SQUID, resulting in increased noise levels in the SQUID output. Based on an rf field of 1 μT, calculations show that we need at least 80 dB of attenuation, the major part of which comes from the orthogonal arrangement of the pickup coil with respect to the rf coils. Further attenuation is obtained with a shunt resistor across the input terminals of the SQUID. Since the Johnson noise current generated by the resistor increases as $R^{-1/2}$, while the cutoff frequency varies as R, care must be taken in choosing a value of resistance that effectively attenuates rf, while not unreasonably increasing the system noise. The same type of behaviour is also characteristic of the other commonly used filtering arrangement, a thin low-conductivity shield placed between the rf coil and the pickup coil.[16] The shunt has the advantages that it can be easily modified, and that there is no loss in filling factor from having the pickup coil outside the rf coils. We are currently investigating other methods of passive rf filtering that do not lead to large increases in system noise.

A useful modification for low field NMR experiments would be the replacement of the lead flux trapping tube with a larger niobium shield. The larger tube would provide higher homogenity over the sample volume, so samples with a narrow intrinsic linewidth would not exhibit extra line broadening due to dc field inhomogenity. Using a niobium tube would permit trapping of larger fields, since the critical field of niobium is much larger than that of lead. We expect that this type of broadband SQUID system, together with pulsed Fourier-transform SQUID arrangements,[17] will make possible a wide range of low frequency magnetic resonance measurements.

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AC03-76SF00098.

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FIGURE CAPTIONS

FIG. 1. Cross section of the low temperature part of the SQUID spectrometer.

FIG. 2. A superconducting flux transformer transfers magnetic flux between the sample and the SQUID. The inductances of the pickup coil, the coupling coil, and the SQUID are L_p, L_c, and L_s respectively. R is the shunt resistance and M_{cs} is the mutual inductance between the coupling coil and the SQUID.

FIG. 3. An overview of the SQUID spectrometer. The components are a) liquid helium cryostat, b) SQUID feedback unit, c) SQUID control unit, d) frequency counter, e) two channel rf synthesizer, f) low pass filter, g) analog to digital converter, h) computer, and i) chart recorder.

FIG. 4. NQR spectrum of boron-11 in 0.20 cm^3 of boron nitride powder, with a dc field of 0.36 mT. This spectrum is the difference between 10 forward and 10 reverse sweeps, each of 100 s duration, using a linearly polarized rf field. The broad resonance near 1.3 MHz, observed in the powder sample but not in a hot-pressed rod, is probably due to $B_2O_3 \cdot xH_2O$.

FIG. 5. Proton NMR spectrum from a single 400 s sweep of propionic acid at 4.2 K, in a field of 9.3 mT. A sample volume of 0.20 cm^3 was used. The transition between states of the same symmetry, at $\omega_o = 395$ kHz, is flanked by transitions between states of different symmetry, at ω_t and $\omega_o + \omega_t$. The tunnel splitting, ω_t, is measured as 210 kHz. Also visible is the $\Delta m = 2$ transition at $2\omega_o$, near 800 kHz. The inset shows the energy levels for the methyl group.

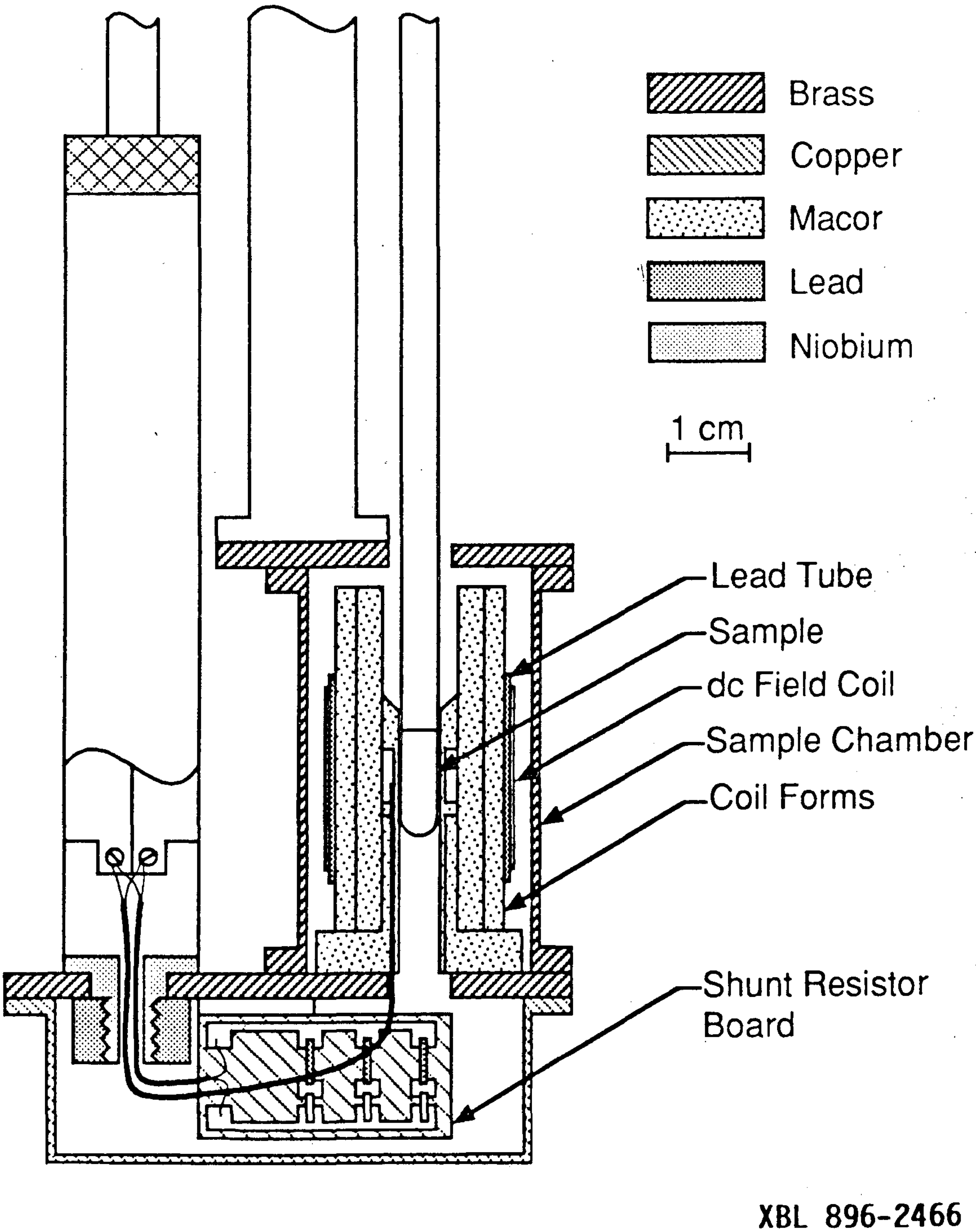
Brass
Copper
Macor
Lead
Niobium
1 cm
Lead Tube
Sample
dc Field Coil
Sample Chamber
Coil Forms
Shunt Resistor Board
XBL 896-2466

Figure 1

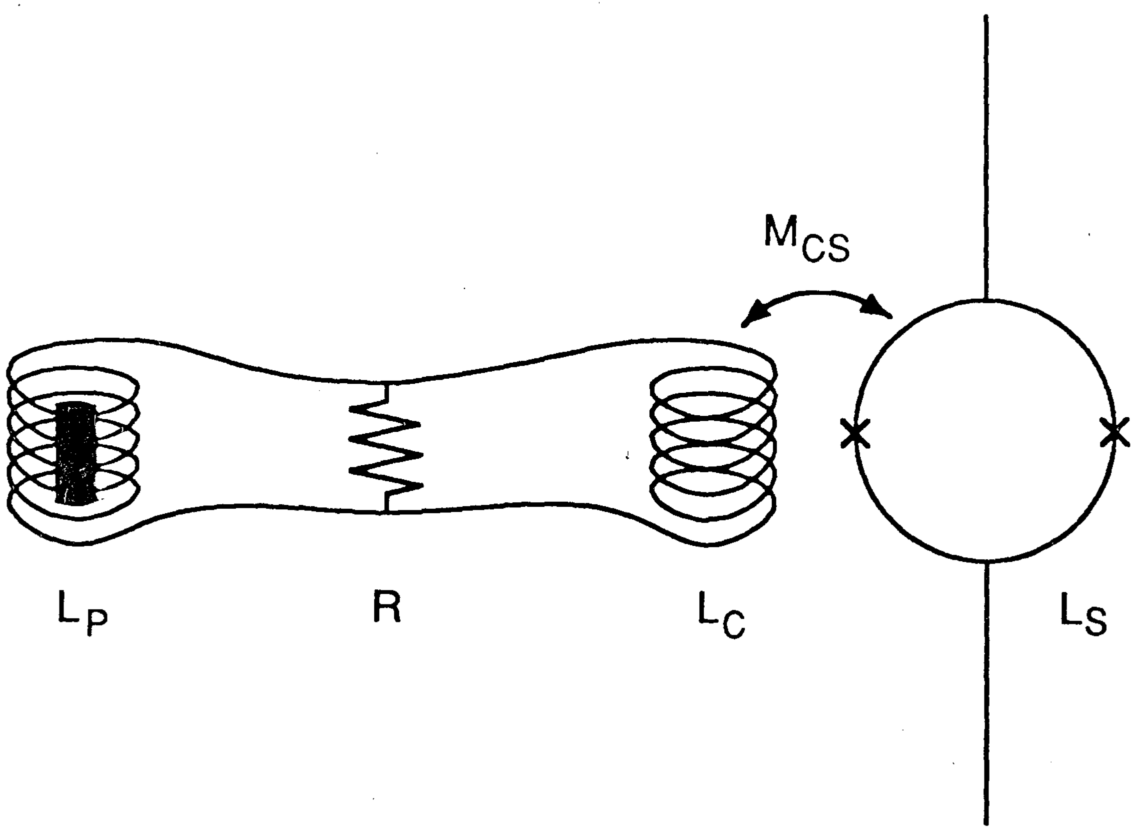

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Figure 2

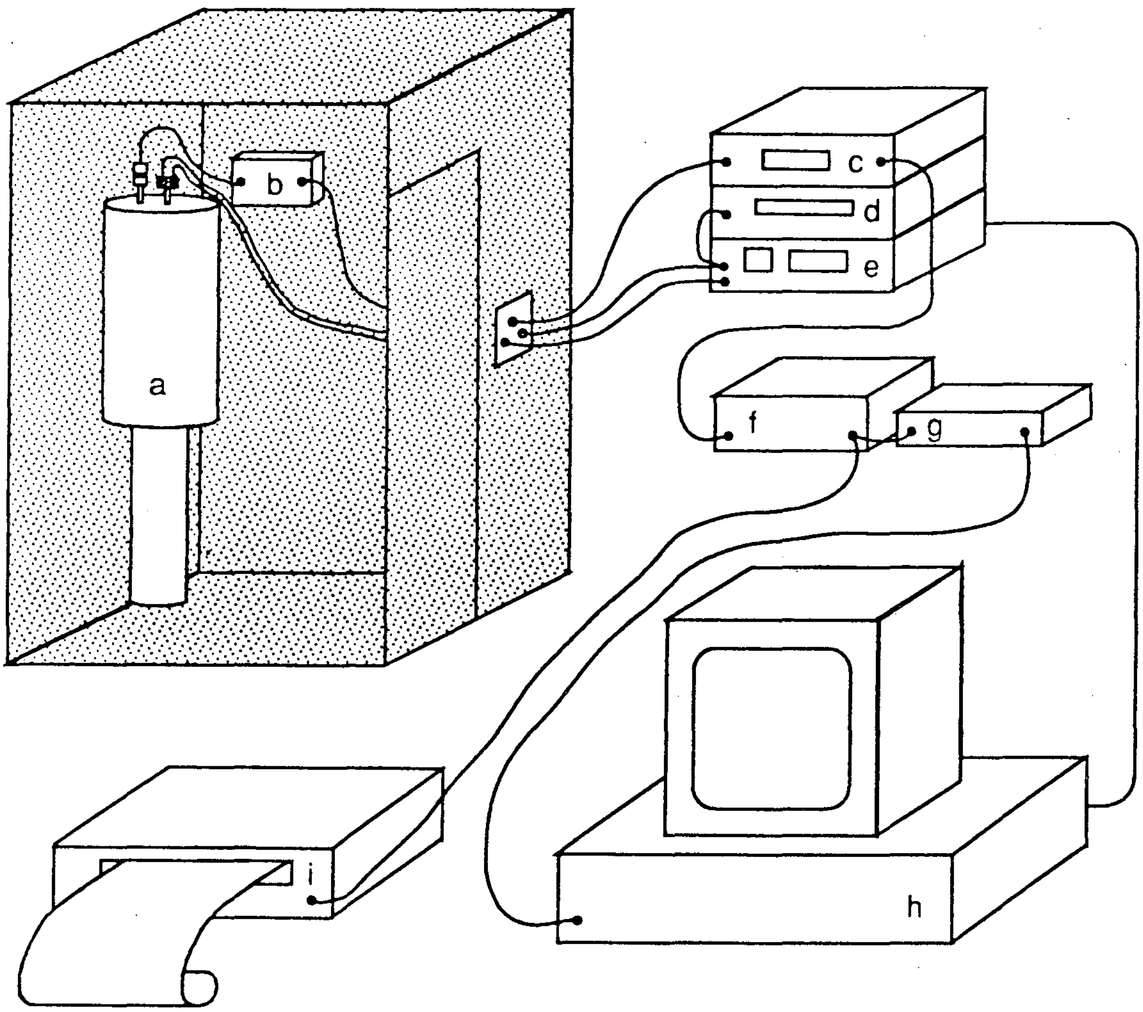

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Figure 3

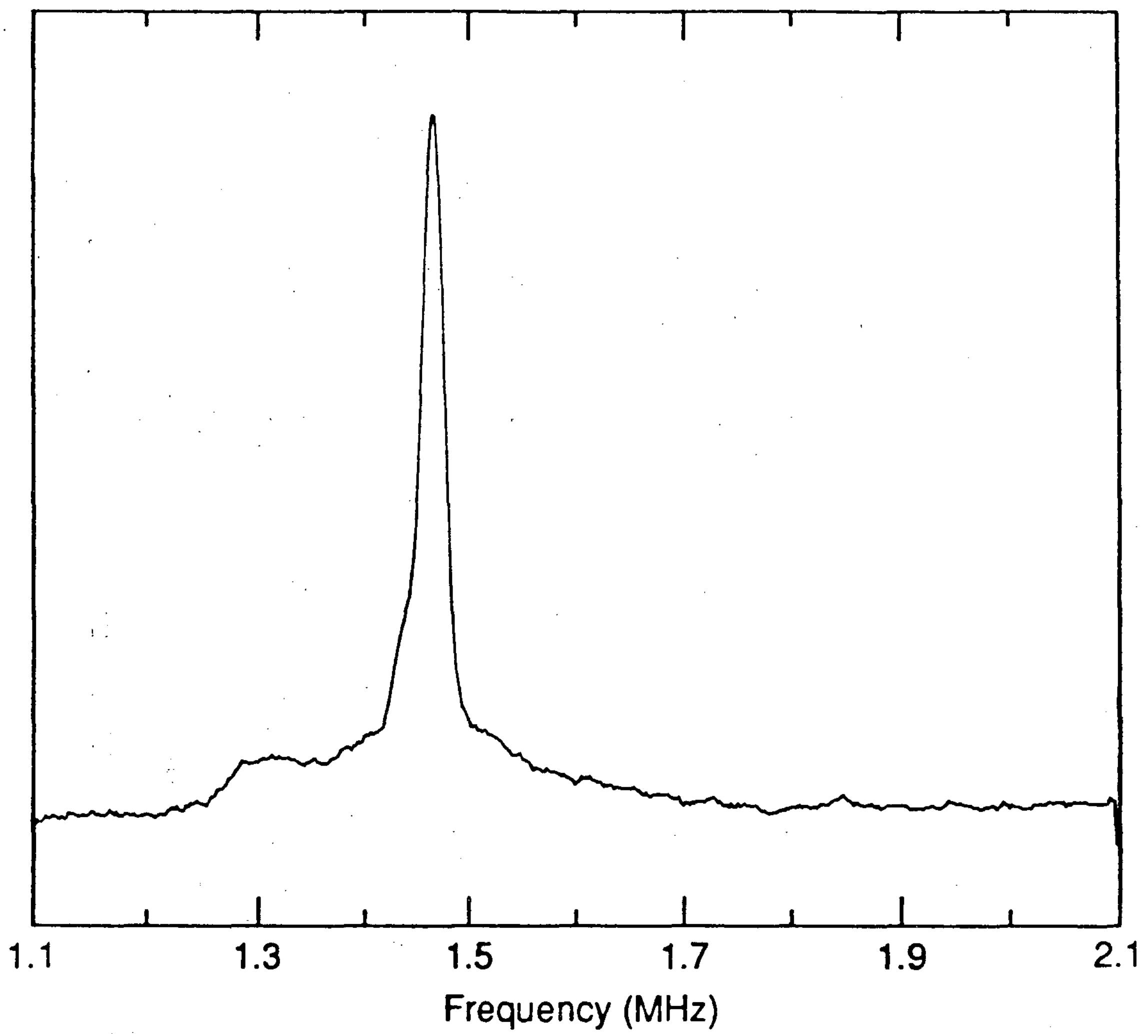

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Figure 4

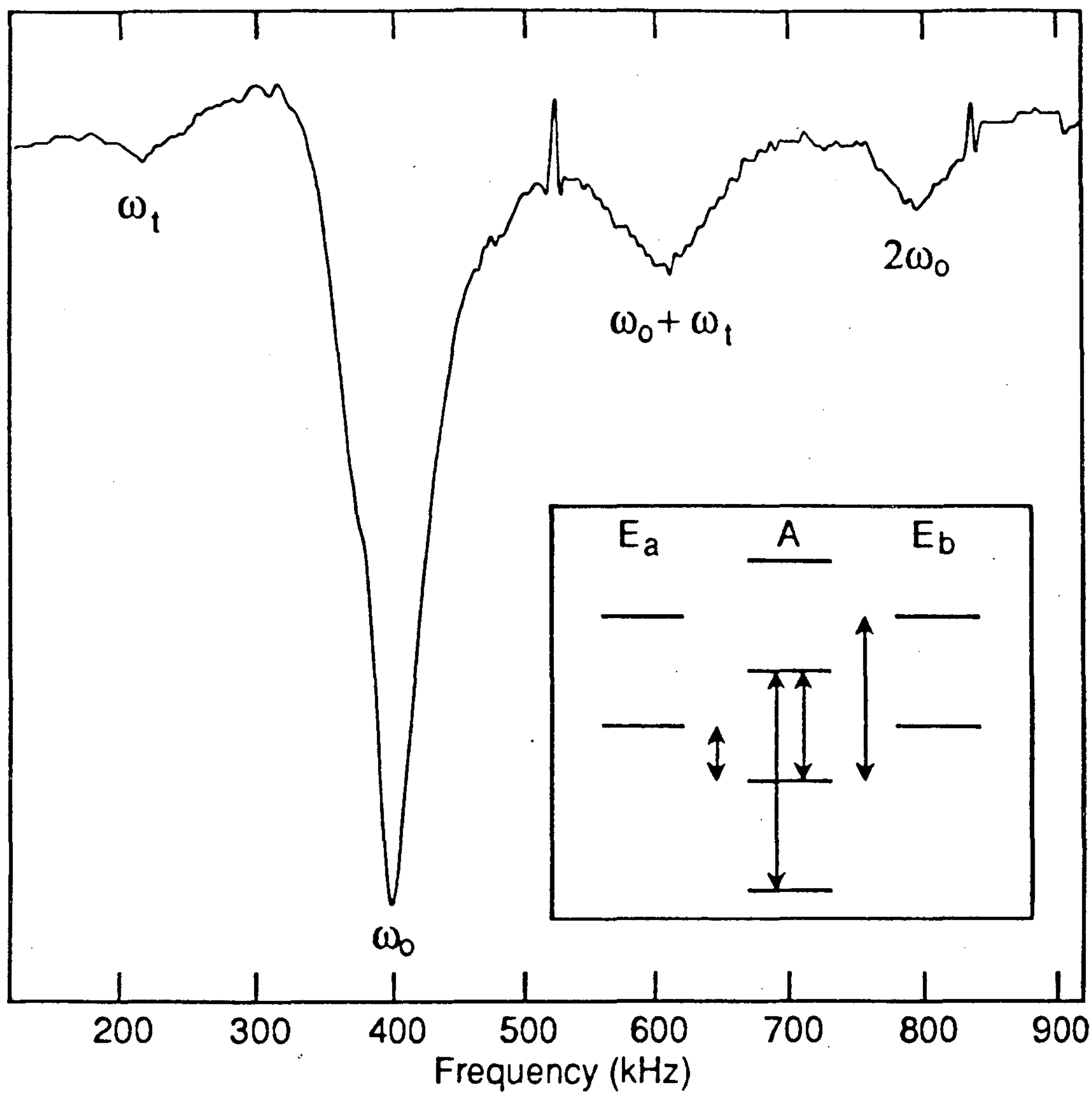

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Figure 5