Fieldfrequency locked Xband Overhauser effect spectrometer

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Field-frequency locked X-band Overhauser effect spectrometer[a)]

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The design and construction of an Overhauser Effect Spectrometer operating at X band is described. The ESR section is a Varian V-4502 spectrometer equipped with a 9-in. electromagnet and a shim coil assembly. NMR detection is based on a broadband rf hybrid juction feeding a coil in an X-band quartz dielectric cavity. Signal processing is carried out at a constant intermediate frequency of 25.1 MHz with a Varian V-4311 fixed frequency rf unit. The mixing scheme employed to translate the NMR information to 25.1 MHz is described. Medium resolution performance (resolution $\sim 10^{-6}$) for the NMR is achieved under field-frequency locked conditions. The lock is based on a Super-Regenerative Oscillator (SRO) housing a control sample, and operating as a field-tracking frequency source. This SRO injects into an oscillator which excites the analytical sample resonance and also serves as a local oscillator, thereby making the locked spectrometer multinuclear in capability. Typical Overhauser effect recordings of protons and fluorines are presented.

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INTRODUCTION

In a system containing unpaired electrons and magnetic nuclei, Overhauser has shown[1] that the saturation of the electron spin resonance can lead to remarkable changes in the NMR signal due to cross relaxation. The Overhauser effect is a manifestation of the dynamic nuclear polarization in the system. Dynamic nuclear polarization (DNP) studies on liquids composed of a diamagnetic solvent and a free radical solute have proved capable of accurately reflecting details of the dynamic processes in solution which have a characteristic time scale of 10^{-8} to 10^{-12} s.[2-4] On the other hand, differential enhancements of chemically shifted resonances in a molecule have proved to reflect the bonding situation accurately: such studies have by and large been confined to nuclei such as ^{13}C and ^{31}P which lie in the interior of a molecule.[5,6] Differential effects exhibited by nuclei such as ^{19}F which lie at the molecular periphery have been the subject of Q-band investigations,[3] where DNP effects tend to be intrinsically small owing to the high electron Larmor frequency. We have therefore been interested in studying such effects at X band, where the resolution and enhancement requirements are not seriously in conflict. To this end, we found it necessary to develop a medium resolution Overhauser effect spectrometer, built around the facilities available in our laboratories.

I. THE SPECTROMETER

A. Probe

The ESR section of the Overhauser effect spectrometer is an X-band Varian V-4502 system equipped with a Hall regulated Varian V-3400 9 in. magnet. ESR is excited by placing the DNP sample in a cylindrical quartz dielectric cavity (unloaded $Q \sim 3000$) operating in the TE_{012} mode,[7] the cavity being connected to the high-power arm of the V-4502 system. The derivative ESR signal could be conveniently displayed by connecting the modulation coils mounted on the sides of the cavity to the 100 kHz modulator of the V-4502 system, 100 kHz phase sensitive detection being a routine facility on the Varian spectrometer. The block diagram of the NMR section of the spectrometer, designed and constructed in our laboratory, is given in Fig. 1. NMR excitation of the DNP sample is achieved by means of a coil connected to arm 1 of a broad band rf hybrid junction which is fed by an rf source at arm H. The NMR coil consists of four turns of 28 S.W.G. enamelled copper wire wound around a quartz former of ~ 5 mm i.d. and 7 mm o.d. The cavity and coil are coaxial, the position of the coil in the cavity being chosen to maximize the DNP response. The use of the dielectric cavity and the thin-wire NMR coil ensure that the introduction of the coil into the cavity does not drastically alter the cavity Q or effectively shield the DNP sample from the microwave field.

B. NMR bridge

A major requirement on the NMR section of the DNP spectrometer is the linearity of the NMR detection system, especially for quantitative DNP measurements. Bridge systems satisfy this requirement reasonably well. In our spectrometer, we have employed (see Fig. 2) a broad band (2–32 MHz) rf hybrid junction.[8] Arm 2, which is one of the side arms, is terminated in a fixed 50 Ω rf termination while arm 1 is connected, as mentioned above, to the NMR tank circuit. The sample coil is resonated by a series combination of capacitors. The use of broadband hybrid junction systems for magnetic resonance has been described previously in the literature
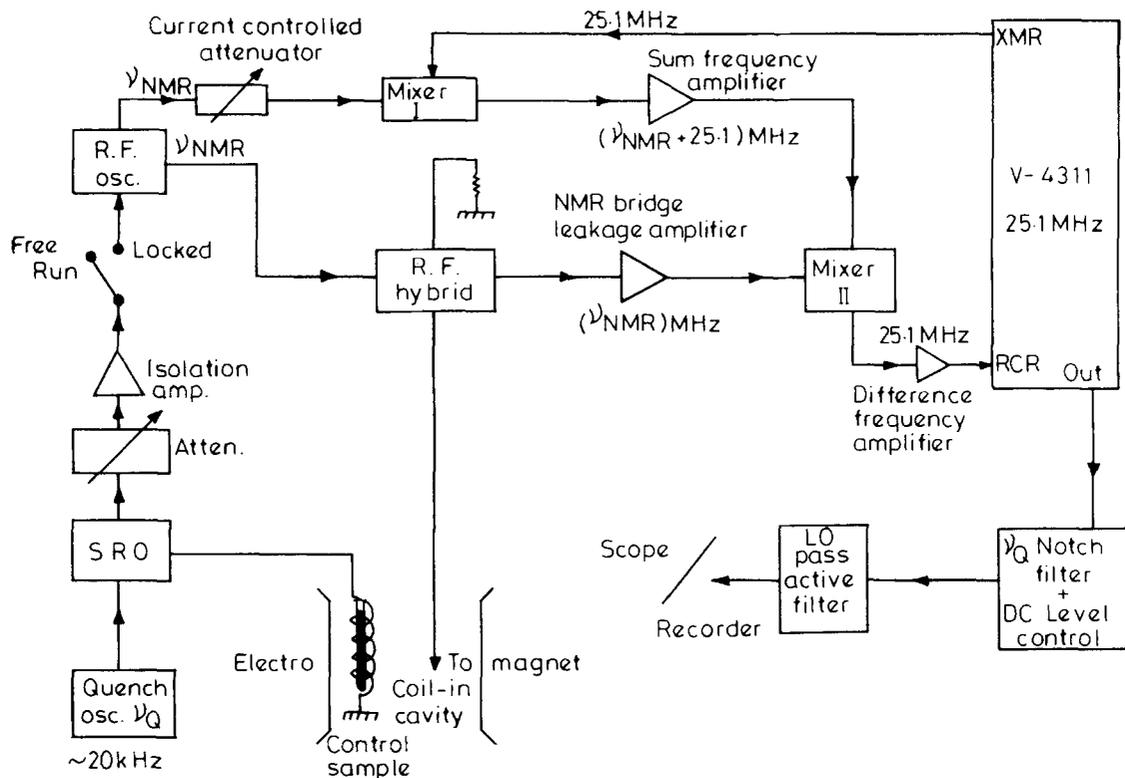
FIG. 1. Block Diagram of the NMR Spectrometer.

by Klein and Phelps.[9] Arms E and H are tuned to the frequency of interest by LC-tuned circuits with split capacitance. The output port E of the bridge is isolated from the following amplifier by a buffer stage which consists of a single BFW 11 FET[10] in the common drain configuration.

C. NMR bridge leakage amplifier

The NMR bridge leakage is amplified following isolation. The amplifier consists of a single LM 371 chip[11]

with split capacitance input and output for impedance matching. The circuit is shown in Fig. 3. The coils L_1 and L_2 are chosen for a resonance frequency equal to ν_{NMR}, the NMR frequency, in conjunction with the respective trimmers C_1, C_2, and C_3, C_4. The bandwidth between 3 dB points is ~1 MHz and voltage gain is ~45.

D. R.F. oscillator

It proved convenient to employ a home-built solid-state oscillatory for exciting the rf bridge. The circuit
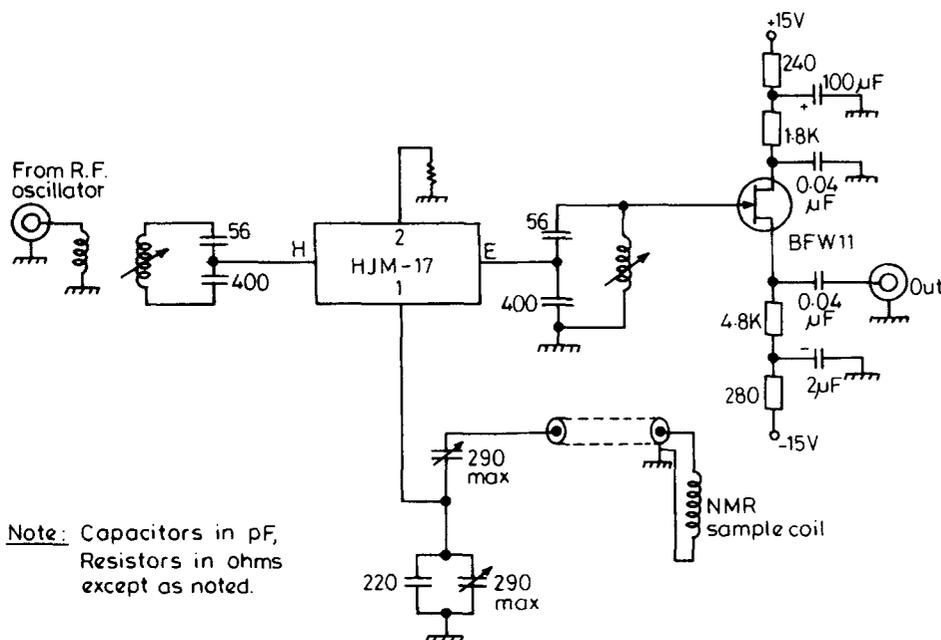

FIG. 2. Details of the NMR Bridge Configuration (HJM-17 is a hybrid junction manufactured by Merrimac R&D, Inc., West Caldwell, NJ 07006 U.S.A. BFW-11 is a FET manufactured by Bharat Electronics Limited, Bangalore, India).
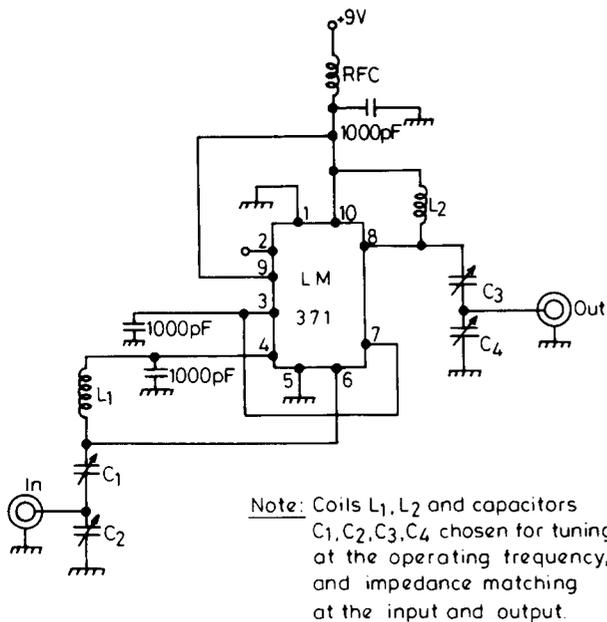
FIG. 3. NMR Bridge Leakage rf Amplifier (The LM 371 chip is an rf Amplifier manufactured by National Semiconductor Corporation, California, U.S.A.).

Note: Coils L_1, L_2 and capacitors C_1, C_2, C_3, C_4 chosen for tuning at the operating frequency, and impedance matching at the input and output.

of this oscillator is shown in Fig. 4. It consists of two 2N4391 FET's in differential configuration for feedback, with the common source grounded through a resistor. The output is taken from the drain of the oscillator FET, and is available at a standard BNC port, a parallel output is fed to a double-balanced mixer (DBM),[12] configured as a current-controlled attenuator. The output from the DBM is available at a standard TNC port. A single-turn coil is wound on the tank coil L and is connected to a standard BNC connector. This port is used for frequency counting or injection.

E. The field-frequency lock unit

The magnetic field control of the V-3400 9 in. electromagnet system was not up to the performance level

required for medium NMR resolution. The deteriorated performance of our ageing electromagnet power supply proved impossible to pin down to specific component failure and hence the need for a field-frequency lock system was keenly felt.

We have employed a simple lock scheme first described several years ago in the literature by Pound and Freeman.[13,14] This scheme employs an SRO as a field-tracking frequency source, which injects into the rf oscillator (described in Sec. 2.4) via the "Injection/Frequency Count" port (see Fig. 4). The SRO used here is of the solid-state variety (Fig. 5). The basic oscillator consists of two 2N4391 FET's in differential configuration, with the current drive provided at the common source by a 2N2369. The quench voltage at ~20 kHz from an oscillator[15] is introduced into the emitter of the 2N995 stage and thus establishes the current drive. This SRO output is coupled out from the drain of the oscillator FET by a buffer stage, amplified by 2N918's and made available at a standard BNC port. The resonant coil of the SRO tank, housing the control sample, is placed in the electromagnet gap, while the box housing the electronics of the SRO itself is kept well outside the magnet. The quench and bias voltages of the SRO are adjusted for the incoherent mode of the SRO, as seen on the oscilloscope. When the magnetic field satisfies the resonance condition of the control sample with respect to a frequency component present in the noise spectrum of the SRO it becomes coherent. The spectrum of the SRO now contains a line which is very close to the Larmor frequency of the nuclear magnetic moment of the control sample. Using the output of the SRO to injection lock the rf oscillator thus establishes field-frequency lock in the analytical channel. The SRO displays two strong primary responses and a number of secondary responses. One of the primary responses is always chosen. A wide-band solid-state amplifier,[16] working on a +15 V power supply is used as the isolation amplifier between the SRO and the rf oscillator. This

Note: 1. L & C chosen for the appropriate frequency.
2. Resistors in ohms, Capacitors in μF except as noted.
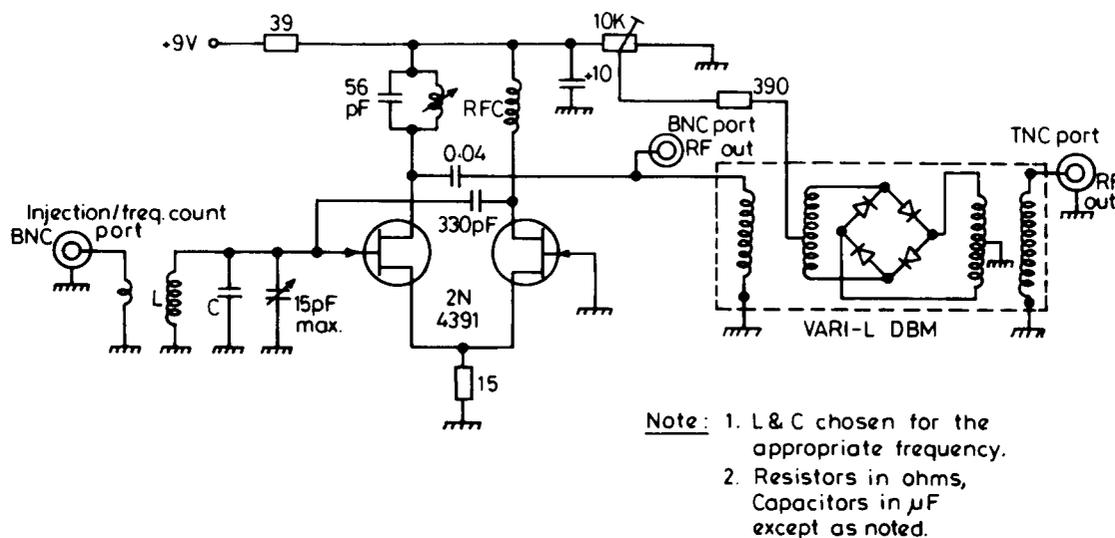
FIG. 4. RF Oscillatory (The VARI-L DBM is a double balanced mixer manufactured by Vari-L, Inc., Denver, U.S.A.).
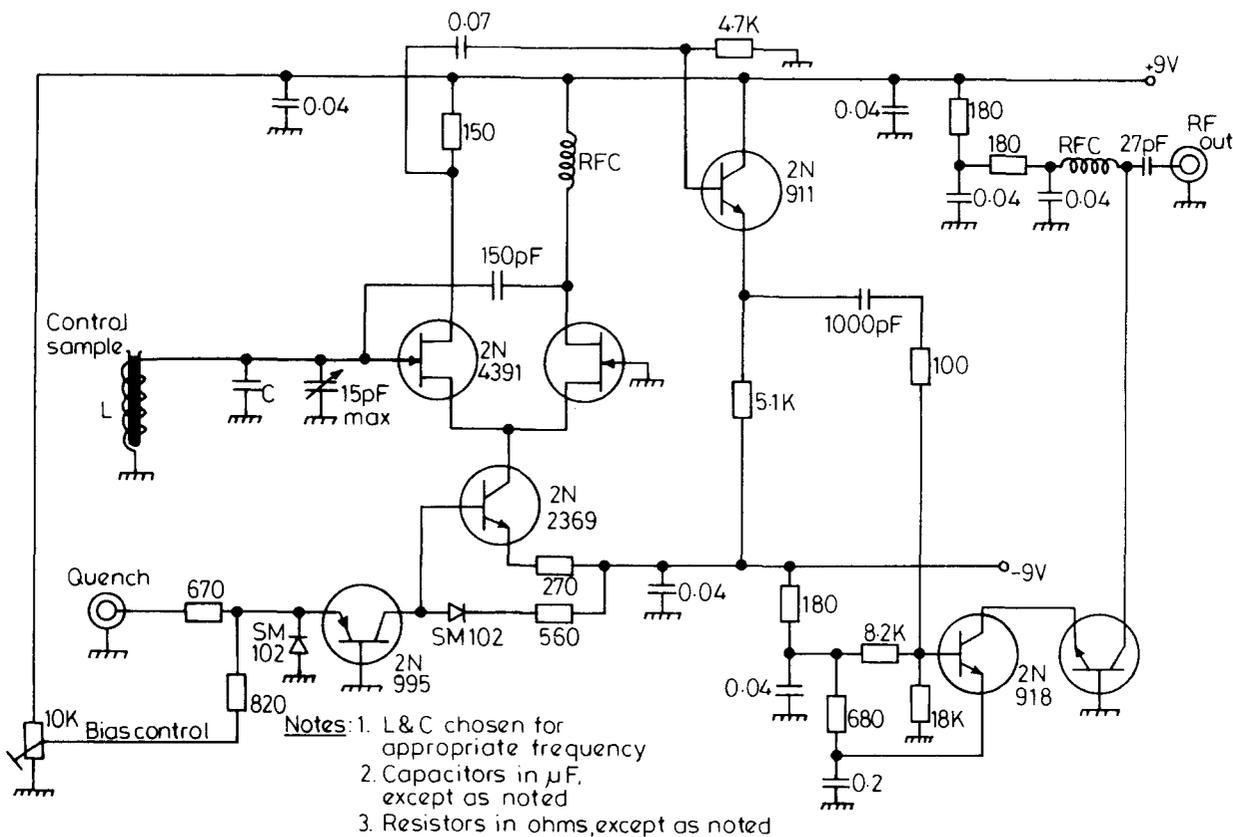
FIG. 5. Super regenerative oscillator.

amplifier has an output dynamic range of ~800 mV into 1 MΩ; in order not to drive the amplifier to saturation, and at the same time to have variable injection level, the SRO output is fed to the amplifier through a 0–99 dB attenuator[17] (dc–100 MHz). The mode of the SRO is very sensitive to radiation in the appropriate frequency range, such as that put out by the rf oscillator. Interference of this nature is avoided by carefully shielding the SRO, particularly the probe housing the control sample. The probe unit we employed was an Alpha NMR probe[7] consisting of a well-shielded rf coil at the end of a one-foot connectorized (standard UHF) metal coaxial tube. After introduction of a sealed ampoule of the control sample [$H_2O/CuSO_4$ for proton studies, and $CF_3COOH/Cu(OAc)_2$ for fluorine studies], the sample-insert hole was also sealed off with a brass cover.

F. NMR detection scheme

NMR signal detection at a constant IF is a desirable feature in an Overhauser effect spectrometer, in view of the interest in multinuclear DNP studies. To this end, we employed a Varian V-4311 fixed-frequency rf unit operating at 25.1 MHz. This unit was originally used as a ^{13}C NMR unit in the Varian HA-100 NMR spectrometer system. It is a transmitter–receiver with rf phase sensitive detection capabilities. Translation of the NMR information to 25.1 MHz was achieved while fully retaining the stability afforded by the field-frequency lock, by employing the mixing scheme shown in Fig. 6. The rf

amplifiers involved in the scheme are both similar to the NMR Bridge Leakage amplifier already described (Fig. 3). The voltage gain of the 25.1 MHz rf amplifier is ~8, while that of the $(25.1 + \nu_{NMR})$ MHz rf amplifier is ~5.

The receiver port of the V-4311 unit is at +300 V, this being the $B+$ required for the tube preamplifier in the Varian system; for the present application, the +300 V supply was disconnected from the "Receiver" port. The output of the receiver unit has a dc component which varies with the receiver gain and phase shifter settings. Upon injection locking, the output also contains a 20 kHz component, since the frequency at which the SRO is quenched is detected under these conditions as amplitude modulation. These dc and 20 kHz components in the receiver output are removed at the dc level control unit. This unit consists of a 741C operational amplifier in standard configuration with a 20-kHz notch filter at the signal input port. A low-pass active filter consisting of two 741C operational amplifiers in standard configuration is also employed following the dc level control unit, to eliminate unwanted line frequency components. The active filter has a sharp cut off at ~20 Hz, and amplifies low-frequency signals to the extent that a 0.1-Hz signal and a 20-Hz signal of equal level at the input are discriminated at the output by ~35 dB. The output of the active filter can be fed to the oscilloscope or recorder. Field sweep for signal presentation is achieved by connecting a function generator[18] (triangle linearity < 1%) to the modulation coils on the cavity. Microwave power
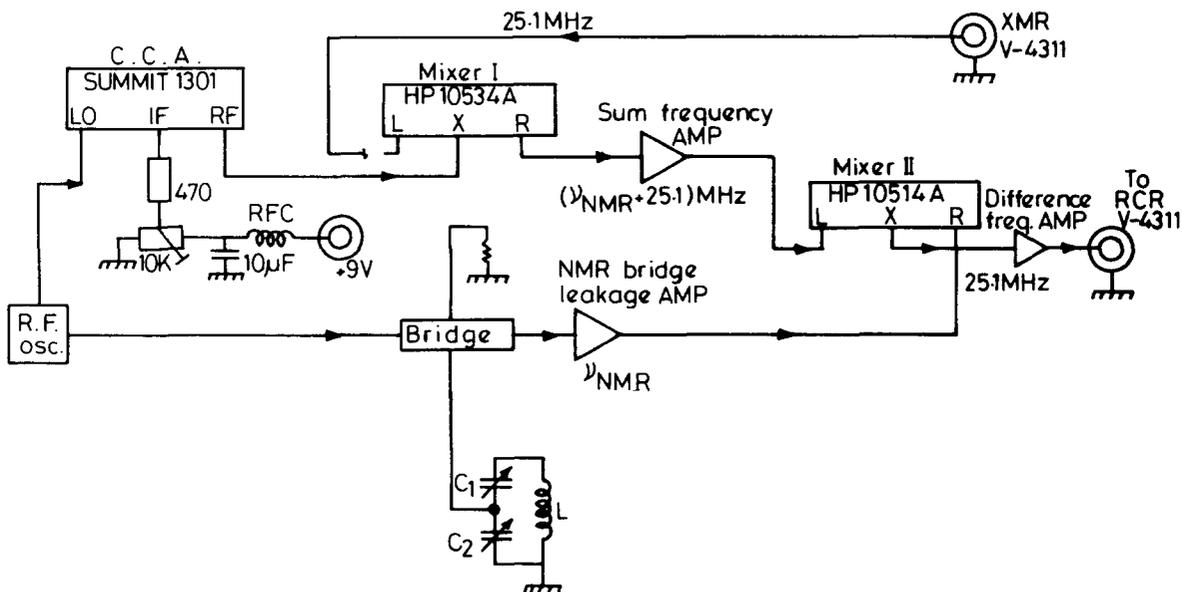
FIG. 6. Mixing Scheme details (C.C.A is a current controlled attenuator. Summit 1301 is a mixer manufactured by Summit Intl. Corp., Salt Lake City, U.S.A. HP10534A and HP10514A are mixers manufactured by Hewlett–Packard, U.S.A.).

is monitored using a precision attenuator connected to the 20 dB port of the Varian Microwave bridge. The precision attenuator we employed is a Waveline Type 612 unit.[19]

The output is detected using a tunable crystal detector mount with 1N23B diode, which is connected following the precision attenuator. This method of power monitoring is based on the fact that the bridge attenuator and precision attenuator are in series, with reference to the crystal detector. The lack of reproducibility of the bridge attenuator in the Varian system is hence of no concern, and the attenuation in dB is read off the calibration chart of the precision attenuator.

II. PERFORMANCE OF THE SPECTROMETER

Figure 7 presents the proton NMR spectra from a 5-mm sample tube containing m-xylene in the presence of ~5 × 10^{-2} M tri-t-butylphenoxyl radical (TTBP) both without and with field-frequency lock. The chemical shift between the aliphatic and aromatic protons is 4.6 ppm in this case. The spectra were recorded after optimizing the magnetic field homogeneity at the sample by adjusting the homogeneity controls of the Varian VK-3532 unit
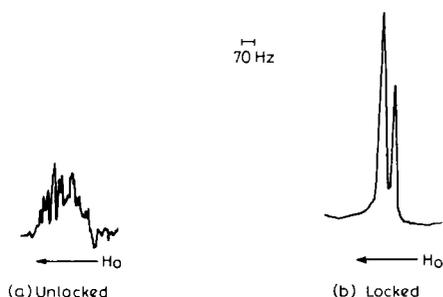
which feeds a set of shim coils mounted on the electromagnet. Sample spinning was not employed. Typical linewidths without sample spinning are ~10 Hz, which is adequate resolution for most DNP studies. Signal-to-noise ratio as measured on the aliphatic peak of a 5-mm sample of neat m-xylene is ~35 : 1.

Under the locked condition, the NMR signal typically remains unshifted to within 100 mG for a 2-G change in the magnetic field. Tracking is more accurate when operating well within this 2-G lock range. The tracking error in the present set up is in large measure due to the displacement of the control sample from the center of the magnet pole gap, which is necessitated by the homogeneity requirements at the analytical sample. This compromise was necessary in our case because the 9 in. electromagnet is equipped with pole faces tapering to 6 in. and has just sufficient gap (~2 in., with shim coils mounted) for the X-band cavity, thus severely limiting the homogeneous region of the magnetic field.

Typical DNP results obtained on this spectrometer are presented in Figs. 8 and 9. In Fig. 8, the equilibrium NMR signal intensity (I_0), of protons in p-xylene with ~5 × 10^{-2} M TTBP has been obtained with the microwave power off, while the enhanced signal intensity

(a) Unlocked   (b) Locked

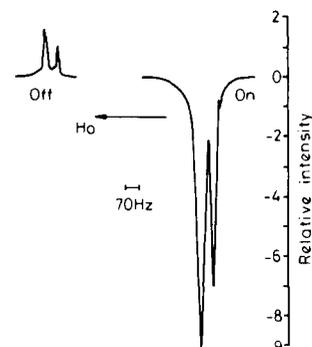FIG. 7. Proton NMR Spectrum of m-xylene/TTBP without (a) and with (b) field-frequency lock.

FIG. 8. Proton NMR spectrum of p-xylene/TTBP sample. Typical ^{1}H Overhauser recordings, with microwave power Off, and On (arbitrary levels) are shown. Radial conc. ~ 5 × 10^{-2} M.
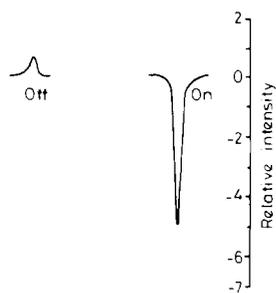
FIG. 9. Fluorine NMR spectrum of 1,4-bis (trifluoromethyl) benzene/TTBP sample. Typical ^{19}F Overhauser recordings with microwave power Off, and On (arbitrary levels) are shown. Radical conc. $\sim 5 \times 10^{-2}$ M.

(I) has been obtained with the microwave power on. Figure 9 shows a similar recording in the case of ^{19}F in C_6H_4 $(CF_3)_2$/TTBP system. Figure 10 presents a typical plot of $-A^{-1} = -[(I - I_0)/I_0]^{-1}$ vs the reciprocal relative microwave power (P^{-1}) applied for this ^{19}F enhancement. The plot is linear, and yields an extrapolated enhancement factor[2-4] of $U_\infty = -71 \pm 9$ (-64) (temperature: $25° \pm 2°$C). Here we have assumed a leakage factor (f) of unity, a good approximation[2-4] at our high radical concentration, where T_1, the nuclear relaxation time in the presence of the free radical, is much smaller than $T_{1,0}$, the relaxation time in the bulk solvent $\{f = [1 - (T_1/T_{1,0})]\}$. This point could be verified with our spectrometer by measuring the solvent nuclear T_1 in the DNP sample with rapid repetitive scan of the NMR signal after suddenly switching off the microwave power subsequent to establishing the DNP. Relaxation times thus measured amounted to a fraction of a second for our samples. The U_∞ value given in brackets has been obtained after Q-enhancement corrections.[20] The U_∞ value at $25° \pm 2°$C obtained on our set up for the system benzene/TTBP is 169 ± 15, after applying the Q-enhancement correction. This compares reasonably well with the literature value[21] of 185 ± 20.
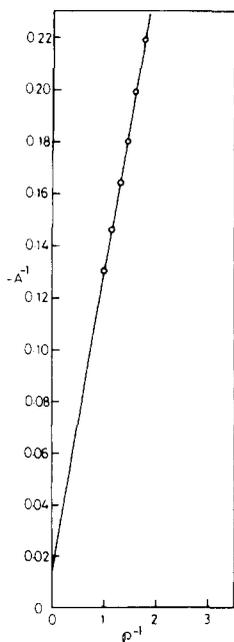
It is to be noted that the maximum microwave power

available from the klystron in the V-4502 system is ~ 300 mW, with even less power reaching the sample in the double resonance probe. This leads to low ESR saturation levels (s ~ 0.1). It is gratifying, however, that in spite of this, the present set up enables reliable extrapolated enhancement factors to be obtained. However, it is clearly advantageous to replace the low-power klystron with a high-power X-band source.

Our spectrometer is multinuclear in capability owing to the following features: (1) it is built around a broadband rf hybrid for NMR detection. (2) Signal detection is at a constant IF of 25.1 MHz, with broadband mixers and tunable amplifiers; the phase sensitive detection capability of the receiver gives an improved S/N ratio. (3) Tuning the SRO and rf oscillator, and using the appropriate homonuclear control sample makes field-frequency locked NMR detection feasible for several nuclei.

The spectrometer is particularly well-suited for medium resolution studies on nuclei such as ^{19}F, which exhibit rather large chemical shifts as compared to protons.

Differential enhancements of chemically shifted fluorine nuclei in several fluorocarbon solvents have been studied in our laboratory employing this spectrometer and these results and their interpretation in terms of molecular orbital theory will be published elsewhere.

ACKNOWLEDGMENTS

FIG. 10. Typical plot of ^{19}F reciprocal enhancement (A^{-1}) vs reciprocal relative microwave power (P^{-1}). System: C_6H_4-$(CF_3)_2$/TTBP.

[a] Based on the Ph.D. thesis of N. Chandrakumar submitted in July '79 and accepted for the Ph.D. degree of the Indian Institute of Technology, Kanpur 208016, India.
[b] To whom all communications should be addressed.
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