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Author
Smith, G.E.

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G. E. Smith, R. E. Blankenship, and M. P. Klein

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CONVERSION OF AN E-3 ESR SPECTROMETER TO 1 MHz FIELD MODULATION

G. E. Smith, R. E. Blankenship, and M. P. Klein
Laboratory of Chemical Biodynamics
University of California
Berkeley, California 94720

ABSTRACT

Conversion of a Varian E-3 ESR spectrometer to 1 MHz magnetic field modulation is described. The normal 100 kHz mode of operation of the instrument is not affected by the modifications. The system has an overall response time of approximately 2 μsec, and has comparable sensitivity to the 100 kHz receiver under similar conditions.

INTRODUCTION

Photophysical and photochemical processes involving free radical or triplet species are often studied conveniently by ESR methods. The kinetic constants of the rise and decay offer unique insights into the mechanisms of production and annihilation. The shortest time constant which can be determined with conventional ESR spectrometers employing 100 kHz magnetic field modulation is ultimately limited to about 10-20 μsec. Faster response times demand either wideband video or superhetrodyne detection, or a higher modulation frequency. The former approaches have been employed effectively[1] but are more demanding of instrumental stability than are the modulation schemes where, in principle, only the sample magnetic susceptibility couples the magnetic field modulation to the microwaves. Fast modulation spectrometers have been described by Atkins <u>et al.</u>[2] and Smaller <u>et al.</u>[3] We were confronted by the problem of photoexcited ESR signals in photosynthetic samples which have been shown to exhibit kinetic constants faster than could be determined in a standard Varian E-3 X-band ESR spectrometer which uses 100 kHz field modulation.[4] The considerations noted briefly above led us to convert this instrument to 1 MHz field modulation, which would shorten the response time by an order of magnitude. We report here the details of the conversion, demonstrate the maintenance of sensitivity for comparable values of field modulation and overall bandwidth, and further demonstrate the extended kinetic range achieved by the conversion.

One of our main objectives was to interfere as little as possible with the conventional mode of operation of this heavily used instrument; thus we elected to construct an independent modulation and detection system which could substitute easily for the standard components. We further elected to leave the microwave components and features unaltered.

Such a conversion involves, minimally, generation and application of the field modulation, amplification of the detected modulation signal, coherent detection, filtering to the extent desired, and finally video amplification to a level sufficient to drive some output device such as a signal averaging computer. Our scheme consists of the additions and modifications shown in Figure 1.

DESCRIPTION

The Varian E-4531 cavity carries a pair of modulation coils, one on either side, connected in series aiding which are tuned to resonance at 100 kHz by capacitors within the 100 KHz driver amplifier. We reconnected the coils in parallel aiding and were able to series resonate them with a capacitance of 596pF whence they exhibited, fortuitously, an impedance of 50 ohms.

As a modulator we used a Hewlett-Packard 467A Amplifier Power Supply which can deliver 10 watts up to a maximum frequency of 1 MHz. Having this unit at hand precluded the necessity of designing and constructing an equivalent unit.

In this section we describe the design goals and criteria of the receiver/demodulator system and provide circuit details for those who may wish to use the system for these or other purposes.

The heart of the conversion is the 1MHz coherent receiver shown schematically in Figure 2. The general layout is straightforward and commonly used. The important difference between this and the similar 100 kHz system is the increased bandwidth of the new system--increased bandwidth being required because the rise-time of the transient response of a system is inversely related to its bandwidth. Our design strategy was to choose a postdetection cutoff frequency which was as high as feasible without sacrificing strong rejection of the 1MHz carrier and to then require that the predetection bandwidth be as narrow as possible without significantly degrading the response established by that post-detection filter. A four-pole 300 kHz Butterworth low-pass filter yields a

10% to 90% rise-time of 1.5 μsec and more than 40 dB of attenuation at 1 MHz. The single-pole selective amplifier reduces the predetection noise bandwidth while, with a Q of 2, maintaining an envelope rise-time of less than 1 μsec. Design and construction of the receiver were simplified by employment of several high-performance components. The Wavetek Model 5080 attenuator provides a 79 dB gain range while introducing negligible phase shift, thus avoiding dephasing the synchronous detector. To accomplish this with an attenuator assembled from discreet resistors, capacitors, and a standard wafer-type rotary switch would require much time and effort. Based on previous experience we used the Hewlett-Packard 10514A balanced mixer as a phase detector. This likewise saved much design time as the detector must respond linearly over a wide dynamic range of signal levels.

A Pierce-type crystal oscillator generates the 1MHz reference wave. Unlike the elaborate reference source in the 100 kHz system, the 1MHz reference amplitude is unregulated. Adoption of this simplification is recommended by Leskovar's analysis which has shown that if the phase detector input signal-to-noise ratio is much smaller than the reference-to-noise ratio, then the output signal is not dependent upon the reference amplitude.[5] Although the ESR signal is strongly dependent upon the modulation amplitude (which is derived from the reference), the resultant stability has been completely satisfactory.

An average responding detector feeding a voltage comparator indicates overload conditions and, in conjunction with an FET switch, protects the mixer.

Two 'L' networks form a lossless power splitter which presents a 50 ohm load to the class C buffer amplifier.

Initially, it seemed that development of an adequate pre-amplification system would bestow unwelcome electrical and mechanical challenges. To interchange amplifiers when switching between 100 kHz and 1 MHz operations would be very inconvenient but it was reasoned that a single wide-bandwidth amplifier, usable at both frequencies, would admit excessive unnecessary noise. Also, while retention of the detector current-monitoring and AFC signal (70 kHz) capabilities of the original pre-amp was mandatory, simply adding a parallel 1 MHz amplifier would compromise, due to source loading, gain and noise performance. Finally, the pre-amp compartment is small and crowded.

Our discovery that the original pre-amp has an upper -3 dB frequency of 900 kHz and more than 33 dB of gain remaining at 1 MHz permitted an easy solution to these problems. Another stage, having 10 dB of midband gain, 50 ohm output impedance, and -3 dB frequencies of 400 kHz and 1.5 MHz has been added following the original amplifier. Operation of the 100 kHz amplifier is undisturbed and a separate 1 MHz output is provided. This circuitry is shown in Figure 3. The additional components were placed in unused space on the original circuit board. Before modification, this board had all otherwise unused pins dedicated to grounding. One of these pins (R) was liberated to be used as the 1 MHz output terminal. The only off-board modifications required were the addition of a type TNC connector to the rear panel and the substitution of 1100 ohm values for the 2700 ohm current limiting resistors which supply pre-amp power.

Performance

Two sets of performance criteria are required. The first is that for standard field-swept experiments the output S/N with 1 MHz modulation is comparable with that attained at 100 kHz for equal modulation amplitude and output filter time-constant. Figure 4 offers such a comparison of the ESR spectra of 4×10^{-5} M $MnSO_4$.

Mn^{+2} was chosen to test the sensitivity of the system because its relaxation time is short compared to the modulation frequency. For samples with a longer relaxation time, attenuation of the signal amplitude is observed at 1 MHz compared to that at 100 kHz. This observation underscores the desirability of retaining the 100 kHz mode of operation for steady state or slow kinetic experiments.

The second criterion is that the kinetic response should be adequate. To perform this test, we employed another balanced mixer as a pulse modulator and gated the field modulation on and off while sitting on a (first derivative) peak of a strong ESR signal. Figure 5a shows the RF current flowing in the modulation coils and Figure 5b shows the associated receiver output. The response is seen to follow closely the excitation which rises exponentially with the 2 μsec time-constant imposed by the resonant modulation circuit.

The true field modulation amplitude on the sample was measured by the line broadening effect of overmodulation. As described in Poole,[6] the observed linewidth is equal to the modulation amplitude if the modulation amplitude is significantly greater than the inherent linewidth of the species being observed. Using an aqueous solution of TEMPO (2,2,4,4 tetramethyl piperidine-oxyl), the modulation amplitude (ΔHpp) was found to be 4 gauss with a 35 V peak-to-peak modulation voltage. This modulation amplitude suffices for most situations we have encountered. If higher amplitudes are sought, care must be taken lest the coils should be destroyed.

As a final indication of the utility of this conversion we show signals obtained from photosynthetic samples exposed to 1 μsec pulses of 600 nm light from a Chromatix CMX-4 dye laser. Observation of these signals required extensive signal averaging. As the time course of these signals is faster than can be acquired by ordinary signal averagers, we employed a Biomation Model 802 as a fast digitizer. This unit is interfaced to a Nicolet NIC-80 computer. This combination is arranged so that after each pass of the Biomation its digital contents are added to the memory of the NIC-80 for as many passes as are required to attain the requisite S/N. In Figure 6 is shown the fastest kinetic component we have observed to date. This signal, which is the subject of a separate paper,[7] is an emission transient. In determining a point-by-point spectrum, we found magnetic field values for which this signal is absent but at which another resonance occurs; thereby eliminating the possibility that we were merely recording a flash artifact. This was comforting as we had been concerned that the AFC system, operating at only 70 kHz, would be unable to compensate for rapid changes in cavity frequency caused by the flash. Apparently these effects are small compared to the signals we are observing.

We conclude with the reminder that if kinetic constants faster than 1 μsec are to be followed and quantitated by ESR measurements it is necessary to reduce the operating quality factor or Q of the sample cavity. Conventional TE_{112} rectangular cavities operate with Q's of about 5,000. Since the time required for the levels of the fields in the cavity to change by e^{-1} are of order 2Q periods of the oscillations, such Q's limit the response to about 1 μsec. Such limitations are well known in the field of pulsed ESR spectroscopy.[8,9]

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Block diagram of elements involved in the conversion of an E-3 ESR spectrometer from 100 kHz to 1 MHz field modulation. An augmented pre-amplifier, placed on the original printed circuit board feeds the coherent receiver indicated within the boxed enclosure. For conventional spectra, the new receiver feeds the instrument's recorder while for transient or kinetic measurements the output filter is reduced to feed an external device.

Figure 2. Schematic circuit diagram of the 1 MHz modulation system.

Figure 3. 1 MHz pre-amplifier modifications. The components shown below the broken line are added. The 1.1 k ohm resistors leading from terminals C and E have been reduced from their original 2.7 k values to accomodate the additional load.

Figure 4. Comparison of the performance at 100 kHz and 1 MHz. The sample was a 4 x 10^{-5} M aqueous solution of $MnSO_4$ contained in a flat cell. In (a) the spectrum taken at 100 kHz. In (b) the same sample observed with the same modulation amplitude and output filter time constant with the 1 MHz system in a duplicate E-4531 cavity. The differences between the two spectra result from some contaminant in the 1 MHz cavity as shown in (c).

Figure 5. Kinetic response of the modified instrument. The Zeeman field was set to a first derivative peak and the field modulation gated on for 25 μsec. Trace (a) shows the current flowing through the modulation coils; the rise and decay times are determined by the

Q of the series resonant circuit. In trace (b) is shown the ESR signal from TEMPO: The rise and decay of the ESR signal closely follow those of the modulation fields.

Figure 6. Kinetic response of a photosynthetic sample to 1 μsec laser excitation pulses. The time width of the ESR signal is limited by the 2 μs response of the system. Although not apparent in this figure, the signal is inverted in sign and thus an emission.

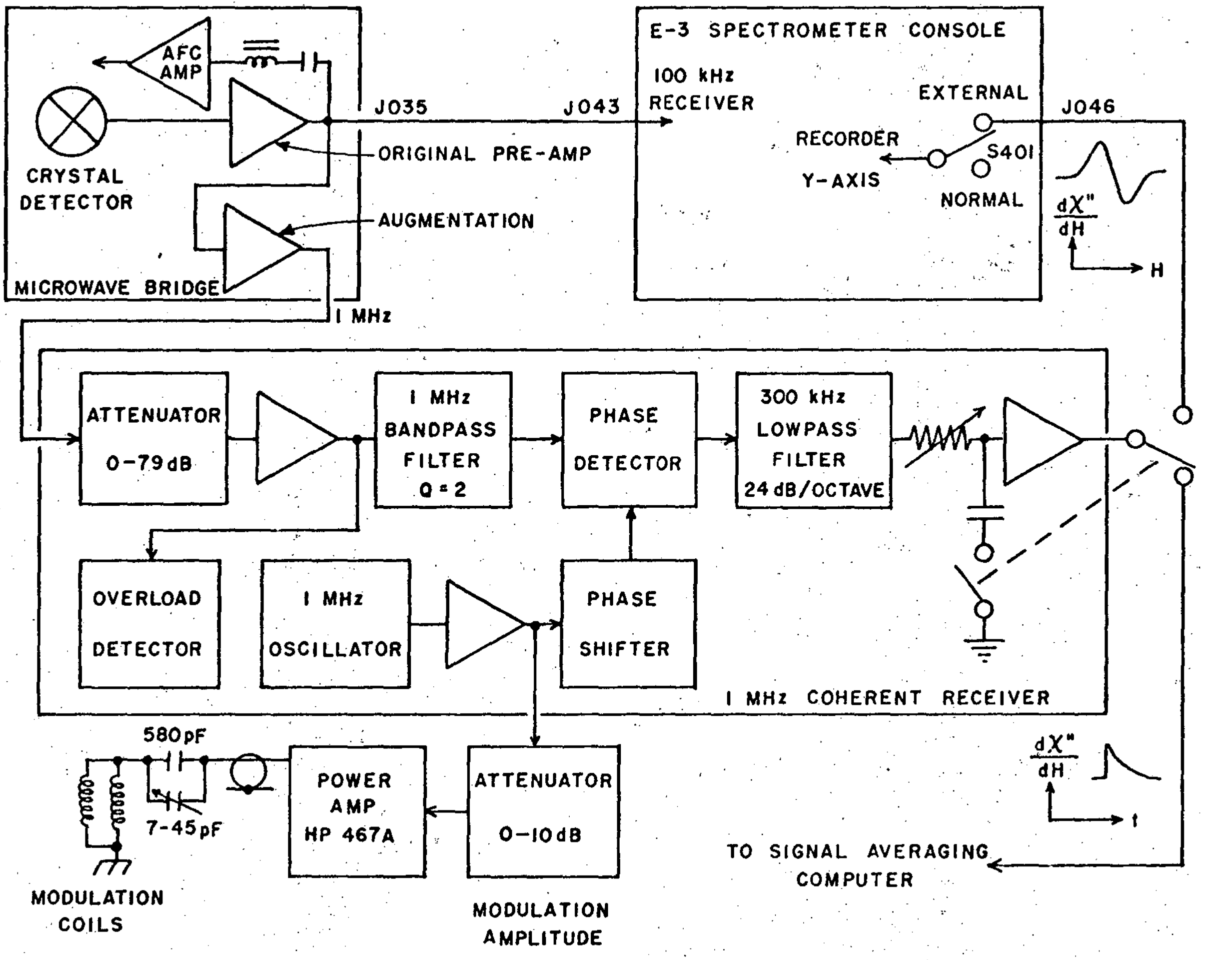

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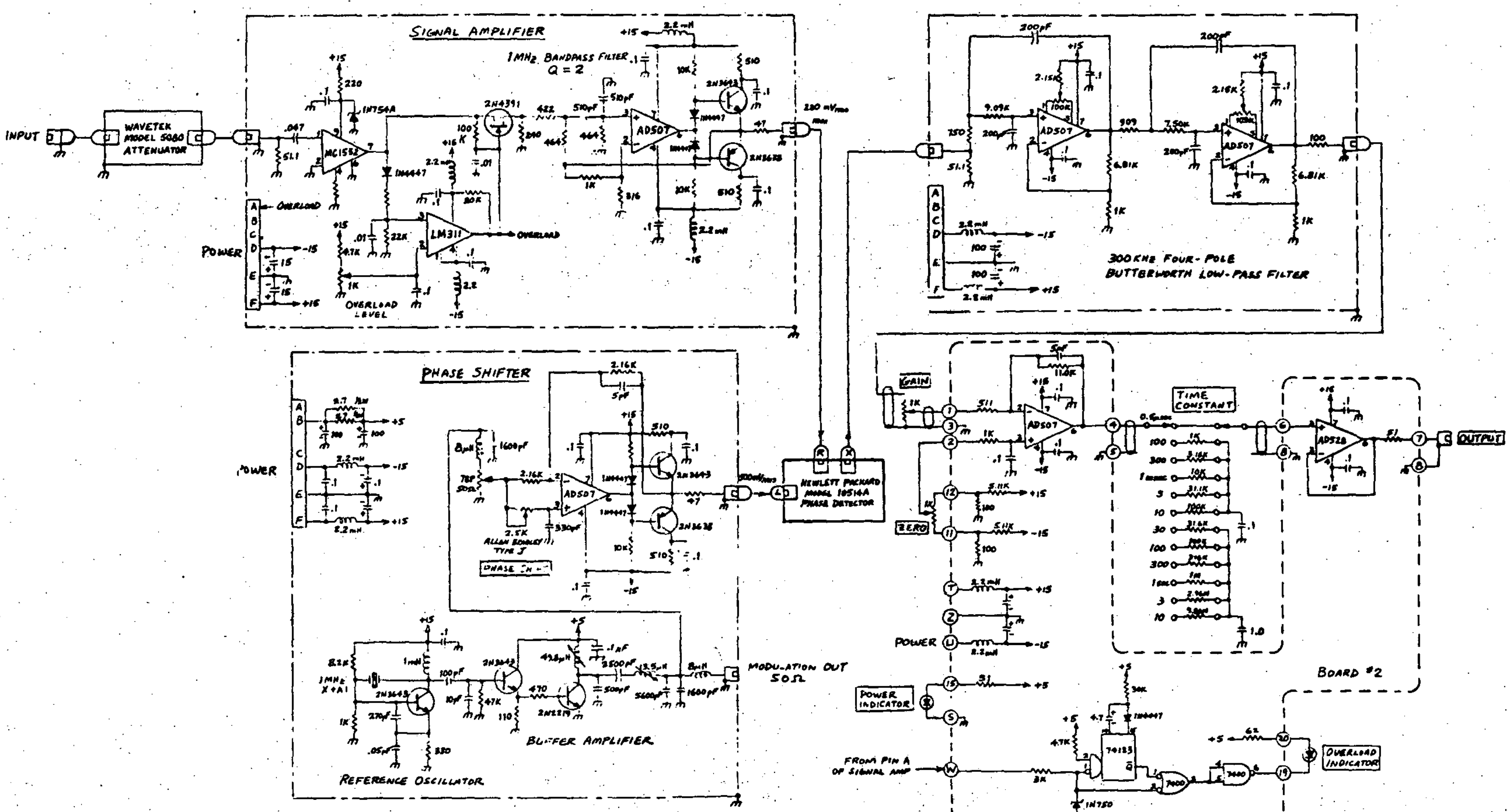
Fig. 1



NOTES: UNLESS OTHERWISE INDICATED
RESISTANCE IN OHMS
CAPACITANCE IN MICROFARADS

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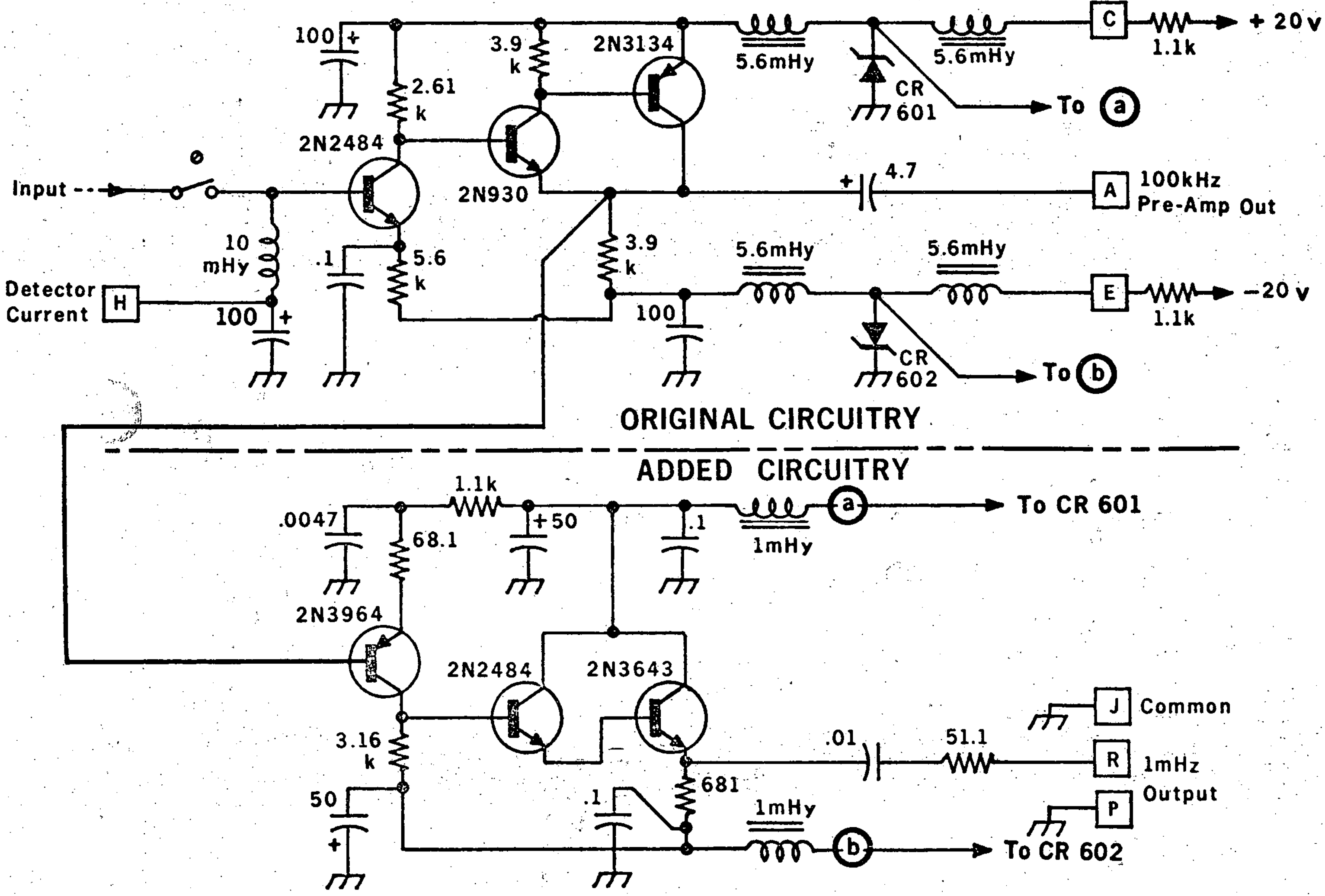
Fig. 2



Capacitance in microfarads

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Fig. 3

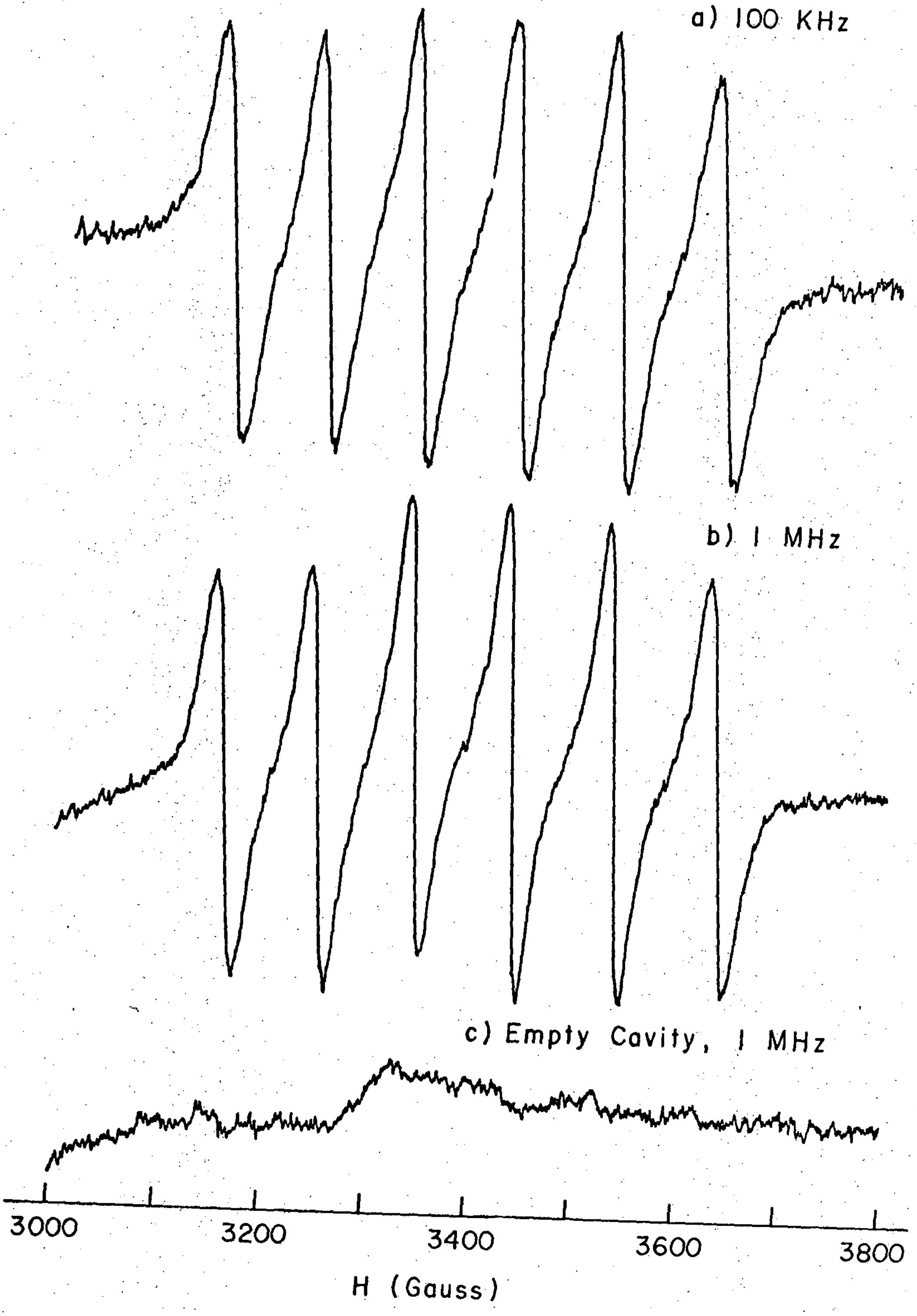

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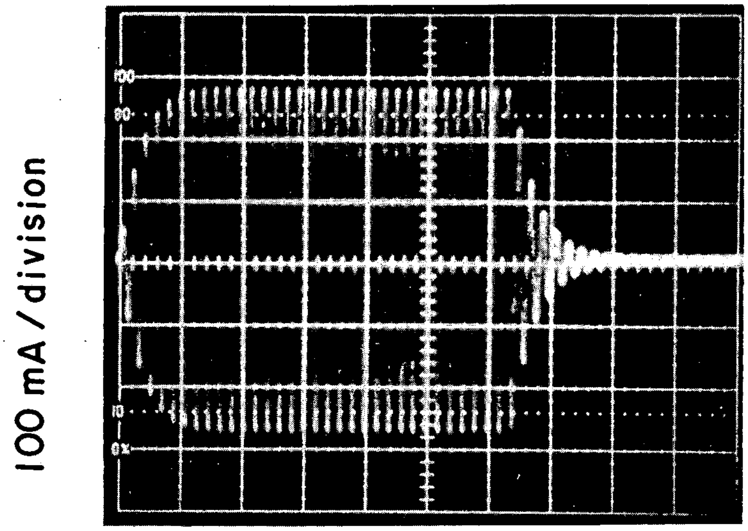
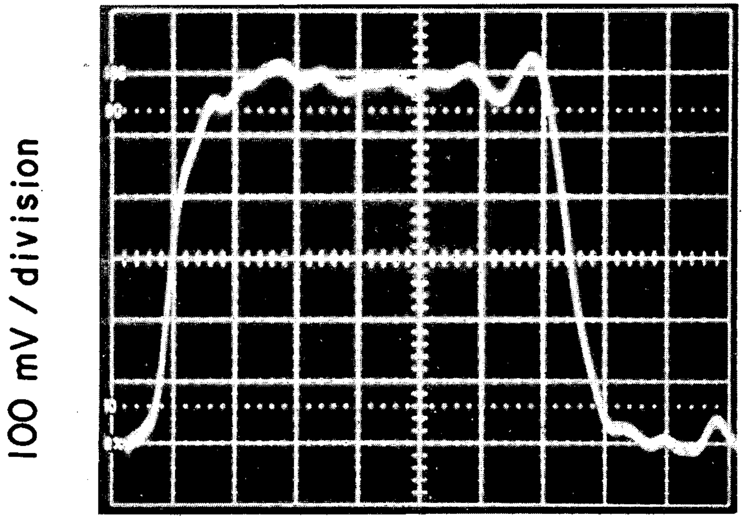
Fig. 4

a) Modulation Current



b) ESR Signal



5 µsec/division

XBB 757-5594

Fig. 5

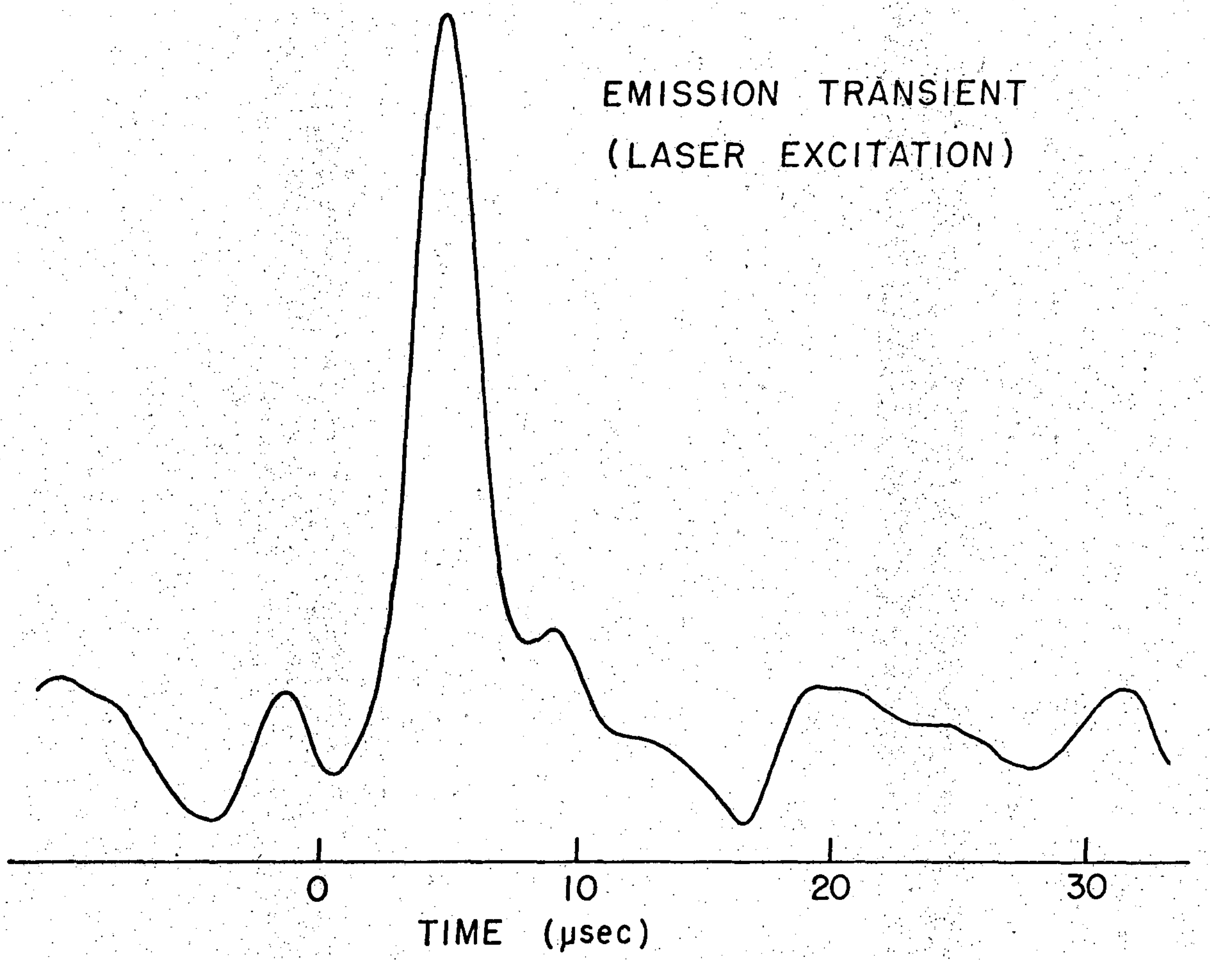


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Fig. 6

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UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720