NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: SPIN DECOUPLING AND INVERSION RATE DETERMINATION

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A Thesis Describing Chemical Research in Ch 80

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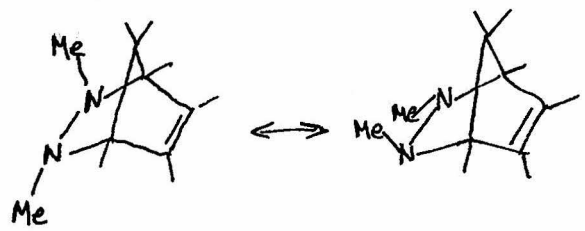
Research Director

Date: May 10, 1968

The technique of spin decoupling (double irradiation) was investigated and developed. Inversion rates for a small bicyclic ring compound were determined as a function of temperature.

The research to be described in this paper was directed primarily toward the solution of two distinct problems. The first was to develop the technique of spin decoupling. Although this technique had been first developed by Bloch in 1954, it had not yet been successfully used at the Institute. The second problem was to determine the inversion rates of the nitrogen atoms in the bicyclic ring (I); NMR spectra over the range +50°C to -40°C were provided.



(I)

The technique of spin decoupling involves the use of two rf fields; one for observation of the spectrum, as in the normal manner, and the other for irradiation of the desired group of nuclei. This irradiation is done at the resonant frequency of the nuclei in question. The object is to cause these nuclei to change states rapidly, causing them to become decoupled from the other nuclei in the molecule; i.e., they no longer cause spin-spin splitting in the peaks of the un-irradiated nuclei.

For these experiments, the Varian HA/HR-60 spectrometer was used. The machine was run in the frequency sweep mode. The principal difficulty in producing decoupling involved adjusting the power output from the rf generator supplying the irradiation field. If the output was too weak, the decoupling effect was too small to be noticed; if the output was too strong, resolution in the remainder of the spectrum was destroyed. Eventually, the method was developed, and decoupled spectra of ethanol and of tetrahydrofuran were produced. Samples of such spectra, together with pertinent information are attached.

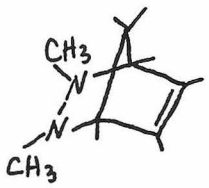
The second part of the research was directed toward determining the rate of inversion of the nitrogens in compound (I). NMR spectra of this compound were available, showing the methyl, vinyl, and bridgehead hydrogens at various temperatures. The procedure used to determine the inversion rates involved feeding the spectral constants (chemical shifts, coupling constants and an assumed τ) into a computer program designated INAB. The shifts and coupling constants were those obtained by analysis of the spectrum using a modified Swalen-Reilly program, NMRIT.

Computed spectra obtained as output from INAB were then compared with the observed spectra and adjustments were made in the value of τ, the lifetime in a given state. The program was then rerun, using the new parameters. This procedure was continued until the computed spectrum was judged to duplicate as nearly as possible the observed spectrum, with regard to peak position, peak height, and linewidths. Matches were thus obtained for all three types of proton at most temperatures. The results

are summarized in Table 1. Values obtained for a given temperature differ slightly among the various groups, due to the difficulties of temperature regulation, but the general agreement is good. Unfortunately, it was discovered after the completion of the analysis that the temperatures reported for the various spectra were incorrect. Thus, no absolute significance can be attached to the results.

I would like to acknowledge the following people for their kind assistance during the course of my research: Dr. John D. Roberts, James Magnuson, and Frank Weigert.

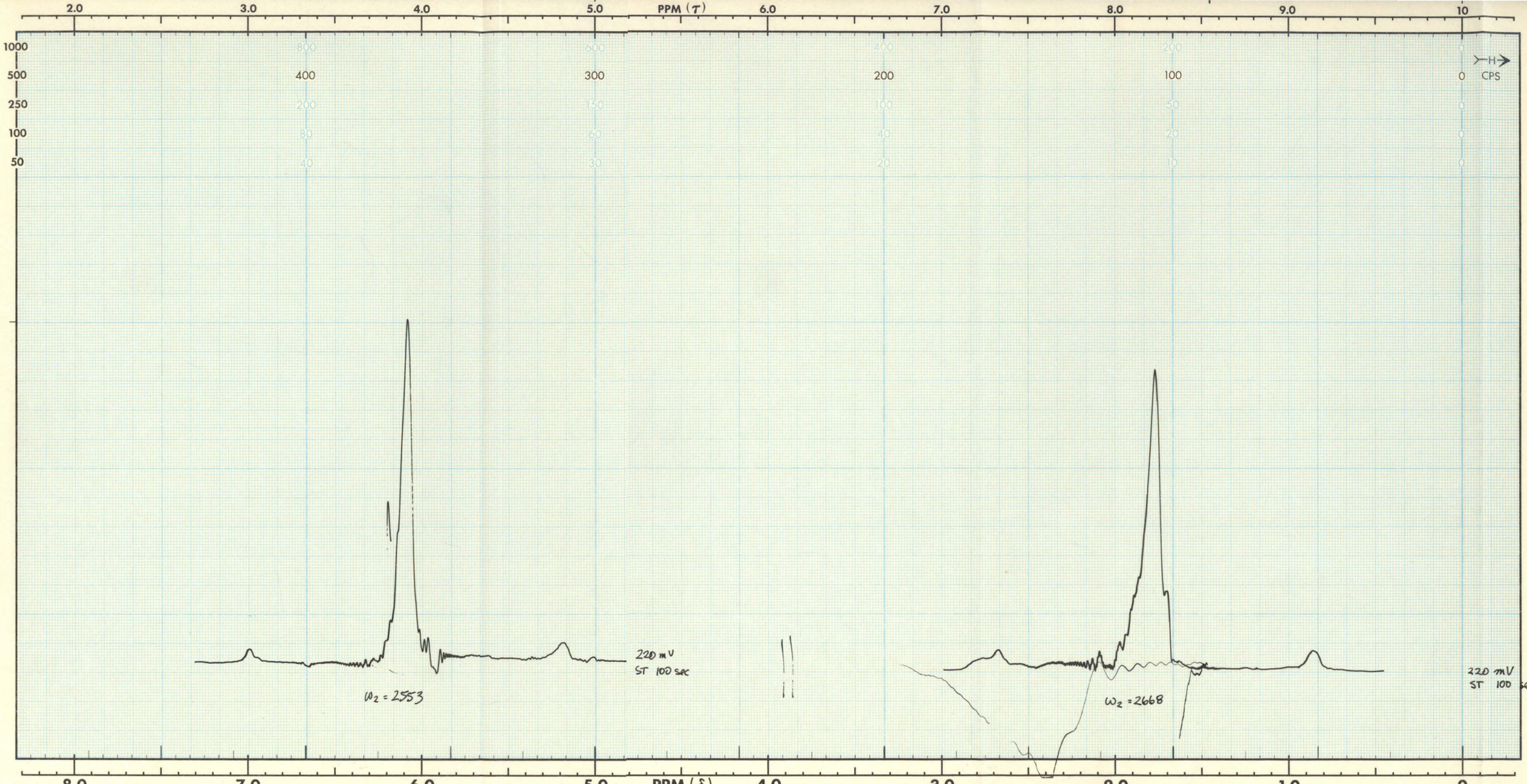
TABLE 1.



T	τ		
	Methyl Hydrogens	Vinyl Hydrogens	Bridghd. Hydrogens
+49.2°C	–	–	–
39.0	–	0.0013	0.00070
31.0	0.0065	0.0055	0.0062
22.8	0.0080	0.0105	0.0100
20.0	–	0.0120	0.0116
17.0	0.0134	0.0134	0.0138
15.0	–	0.0140	0.0150
12.5	–	0.0160	0.0175
11.2	0.0193	0.0193	0.0210
10.0	0.0200	–	–
8.0	0.0242	–	–
7.0	–	0.0260	–
6.0	0.0320	–	–
4.0	0.0350	–	–
1.5	–	0.0370	–
-1.5	0.0433	0.0550	0.045
-12.0	0.152	0.100	0.125
-21.0	0.250	0.250	0.200
-31.0	0.300	0.500	0.250
-40.2	0.500	0.600	0.275

SELECTED NMR SPECTRA

(Additional spectra were submitted to Dr. Roberts at the conclusion of the research project.)



HA-60/DA-60 SPECTRUM

60 MC NMR
SPECTRUM NO.

OPERATOR: MK DATE 7/8/66

SAMPLE: THF, decoupled

SOLVENT:	benzene	benzene	
TEMPERATURE	RT	RT	°C
R.F. FIELD ATTEN.	20	20	db
RECEIVER GAIN	1	1	
FREQ. RESPONSE	20	20	cps
INPUT LEVEL	200	200	
OUTPUT LEVEL	.02	.02	
SWEEP TIME	100	100	sec
SWEEP WIDTH	250	250	cps
SWEEP OFFSET	395	395	cps
REMARKS:			

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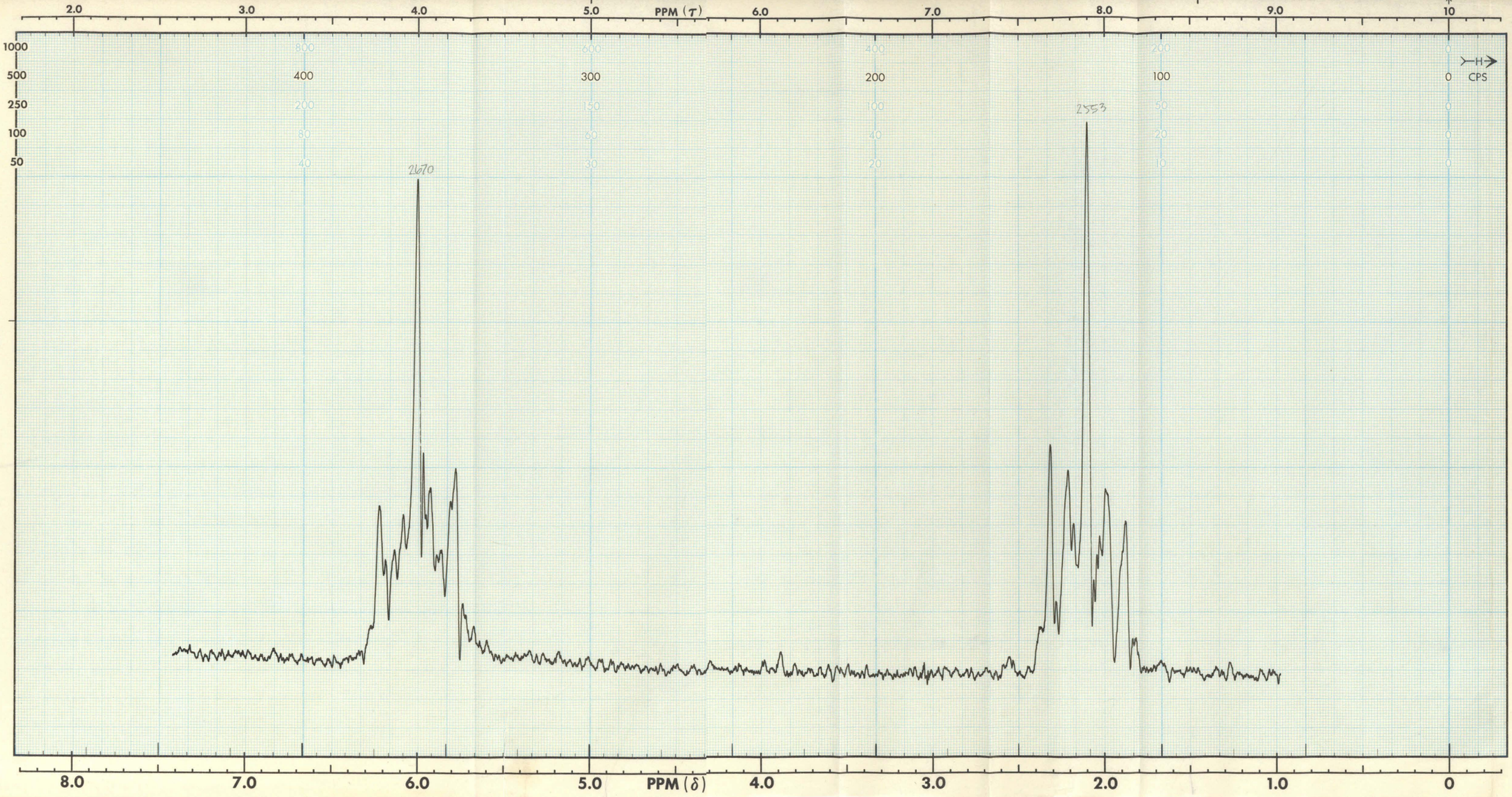

HA-60/DA-60 SPECTRUM

60 MC NMR
SPECTRUM NO.

OPERATOR: MK DATE 7/8/66

SAMPLE: THF and benzene

SOLVENT:						
TEMPERATURE	RT					°C
R.F. FIELD ATTEN.	63					db
RECEIVER GAIN	1					
FREQ. RESPONSE	20					cps
INPUT LEVEL	355					
OUTPUT LEVEL	0.15					
SWEEP TIME	250					sec
SWEEP WIDTH	250					cps
SWEEP OFFSET	395					cps

REMARKS: freq sweep; lock on ②

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HA-60/DA-60 SPECTRUM

60 MC NMR
SPECTRUM NO.

OPERATOR: JK DATE 7/6

SAMPLE: $EtOH$, HCl

- CH_3 peak, while irradiating different areas of the - CH_2 - peak

SOLVENT:				
TEMPERATURE				°C
R.F. FIELD ATTEN.	25			db
RECEIVER GAIN	1			
FREQ. RESPONSE	20			cps
INPUT LEVEL	190			
OUTPUT LEVEL	103			
SWEEP TIME	250			sec
SWEEP WIDTH	500			cps
SWEEP OFFSET	480			cps
REMARKS:				

W_2 = 120 mv @ indicated frequencies

2707 cps

2696 cps

2686 cps

2700 cps

2693 cps

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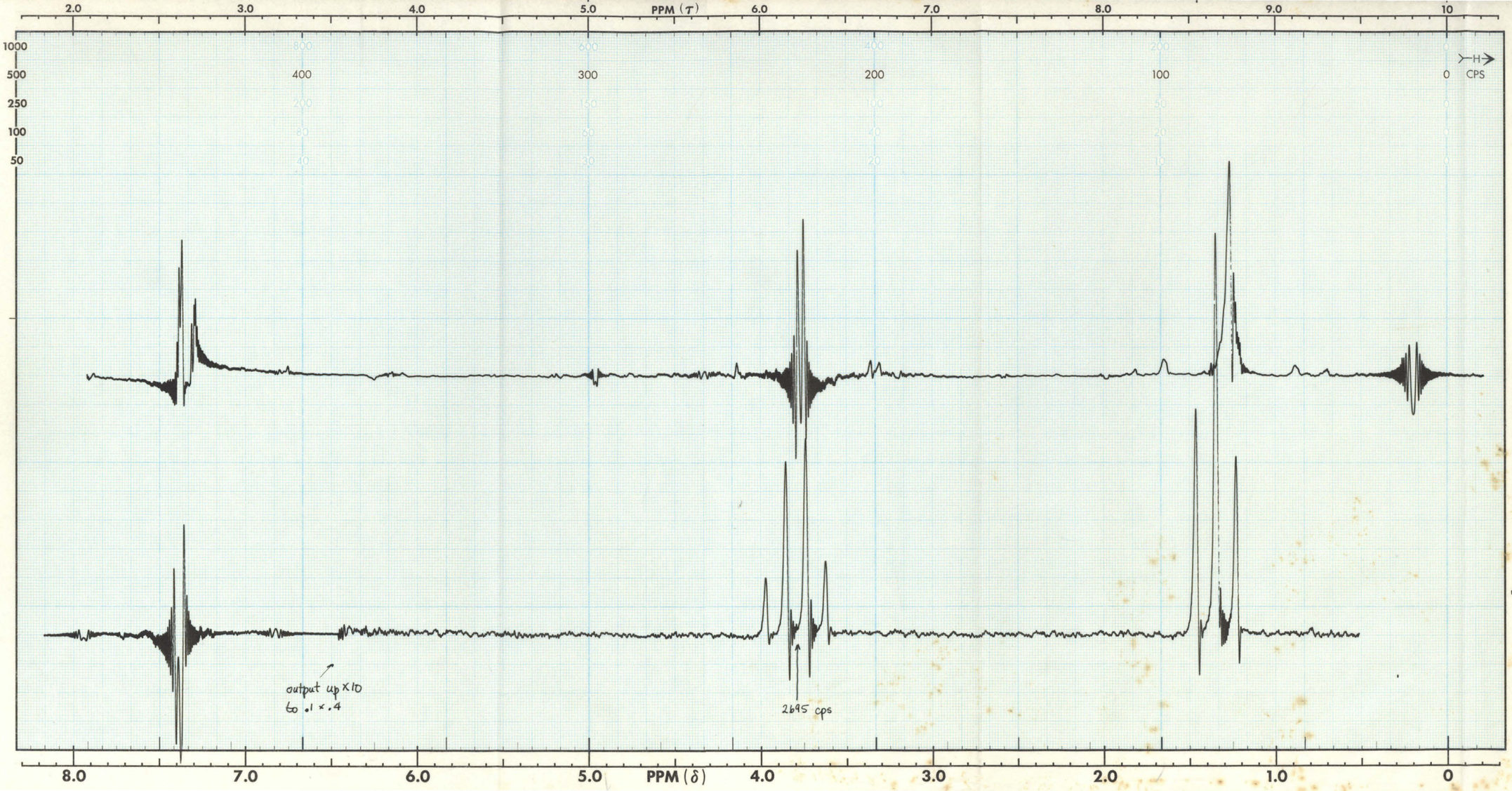

HA-60/DA-60 SPECTRUM

60 MC NMR
SPECTRUM NO.

OPERATOR: MK DATE 7/6/66

SAMPLE:

EtOH + HCl

Top: decoupled; irradiating CH_2 protons

Bottom: undecoupled

	normal	decpl	
SOLVENT:			
TEMPERATURE	rm	rm	°C
R.F. FIELD ATTEN.	56	20	db
RECEIVER GAIN	1	1	
FREQ. RESPONSE	20	20	cps
INPUT LEVEL	190	190	
OUTPUT LEVEL	.1 × .4	.1 × .4	
SWEEP TIME	250	250	sec
SWEEP WIDTH	500	500	cps
SWEEP OFFSET	430	430	cps

REMARKS:

normal
- freq sweep
- man. osc field : 0.6 mG
- sw freq field 0.3 mG
- SA 9000
- freq 2500 cps

decpl'd
- man osc field .03 mG
- sw. fr. field 0.3 mG
- SA 700
- ω_2 : 60 mV p-p @ 2.696 kc

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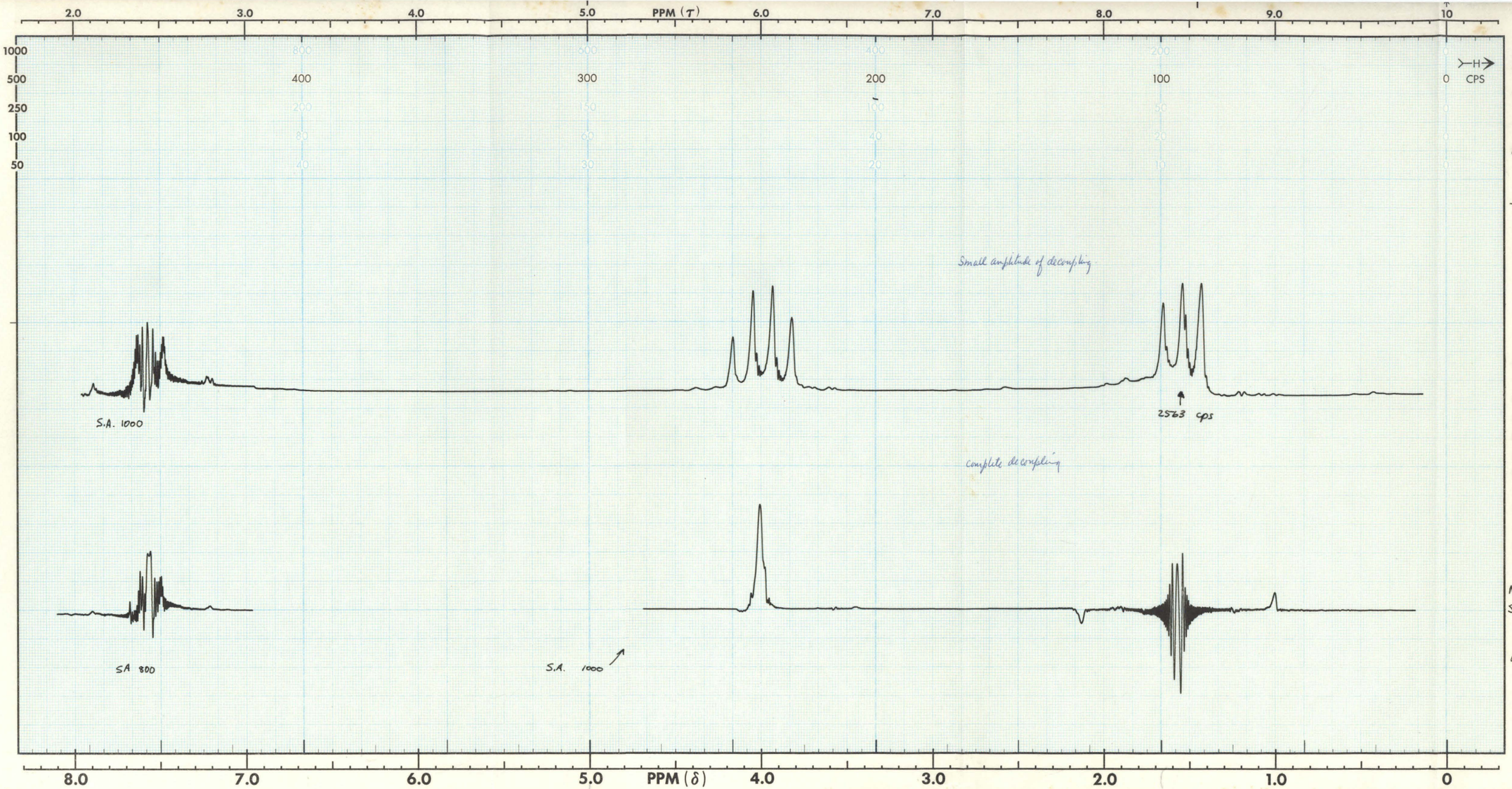

HA-60/DA-60 SPECTRUM

60 MC NMR
SPECTRUM NO.

OPERATOR: MK DATE 7/6/66

SAMPLE:

EtOH, HCl

Top: undecoupled
Bottom: decoupled; irradiating CH_3 protons

SOLVENT:					
TEMPERATURE	rm				°C
R.F. FIELD ATTEN.	19				db
RECEIVER GAIN	1				
FREQ. RESPONSE	20				cps
INPUT LEVEL	190				
OUTPUT LEVEL	.01 ≤.9				
SWEEP TIME	250				sec
SWEEP WIDTH	500				cps
SWEEP OFFSET	441				cps

REMARKS: frequency sweep

M.O. field 10 x .001 mG
S.F. field 3 x 1 mG

ω_2 : 130 mV, p-p @ 2562 cps

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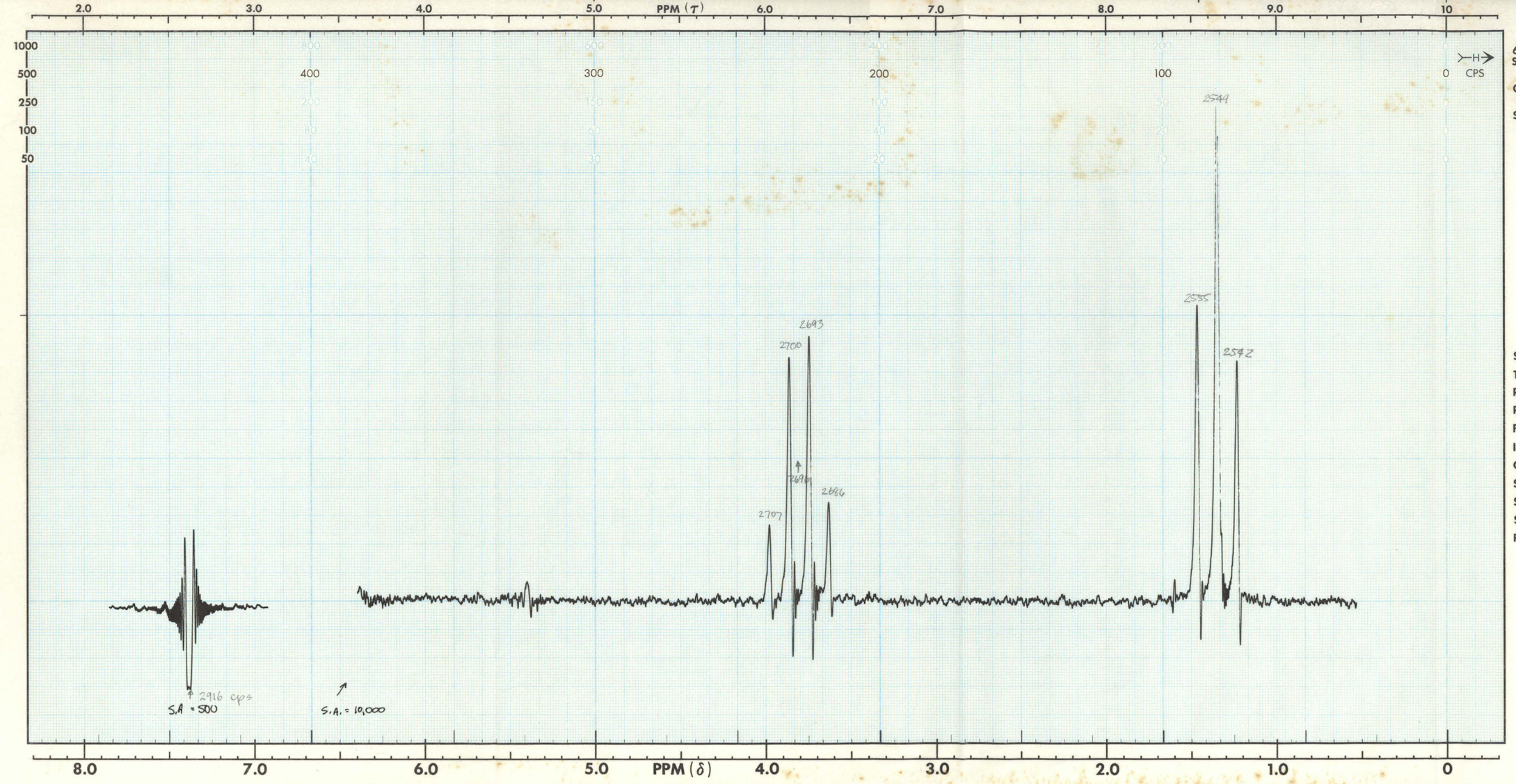

HA-60/DA-60 SPECTRUM

60 MC NMR SPECTRUM NO.

OPERATOR: MK DATE 7/6/66

SAMPLE: EtOH, HCl

Undecoupled

SOLVENT:				
TEMPERATURE	rm			°C
R.F. FIELD ATTEN.	60			db
RECEIVER GAIN	1			
FREQ. RESPONSE	20			cps
INPUT LEVEL	190			
OUTPUT LEVEL	0.07			
SWEEP TIME	250			sec
SWEEP WIDTH	500			cps
SWEEP OFFSET				cps

REMARKS:

freq. sweep 2500 cps
offset 430 cps

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