Texas A&M University

N-M-R Newsletter

No. 194

November, 1974

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Deadline Dates: No. 195: 2 December 1974
No. 196: 6 January 1974

All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843 U.S.A.

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Professor Bernard L Shapiro
Texas A & M University
College of Science
Department of Chemistry
College Station
TEXAS 77843

Your ref	Our ref	Tel ext	Date
	DG/RB	7-462	14 Oct 1974

Dear Professor Shapiro,

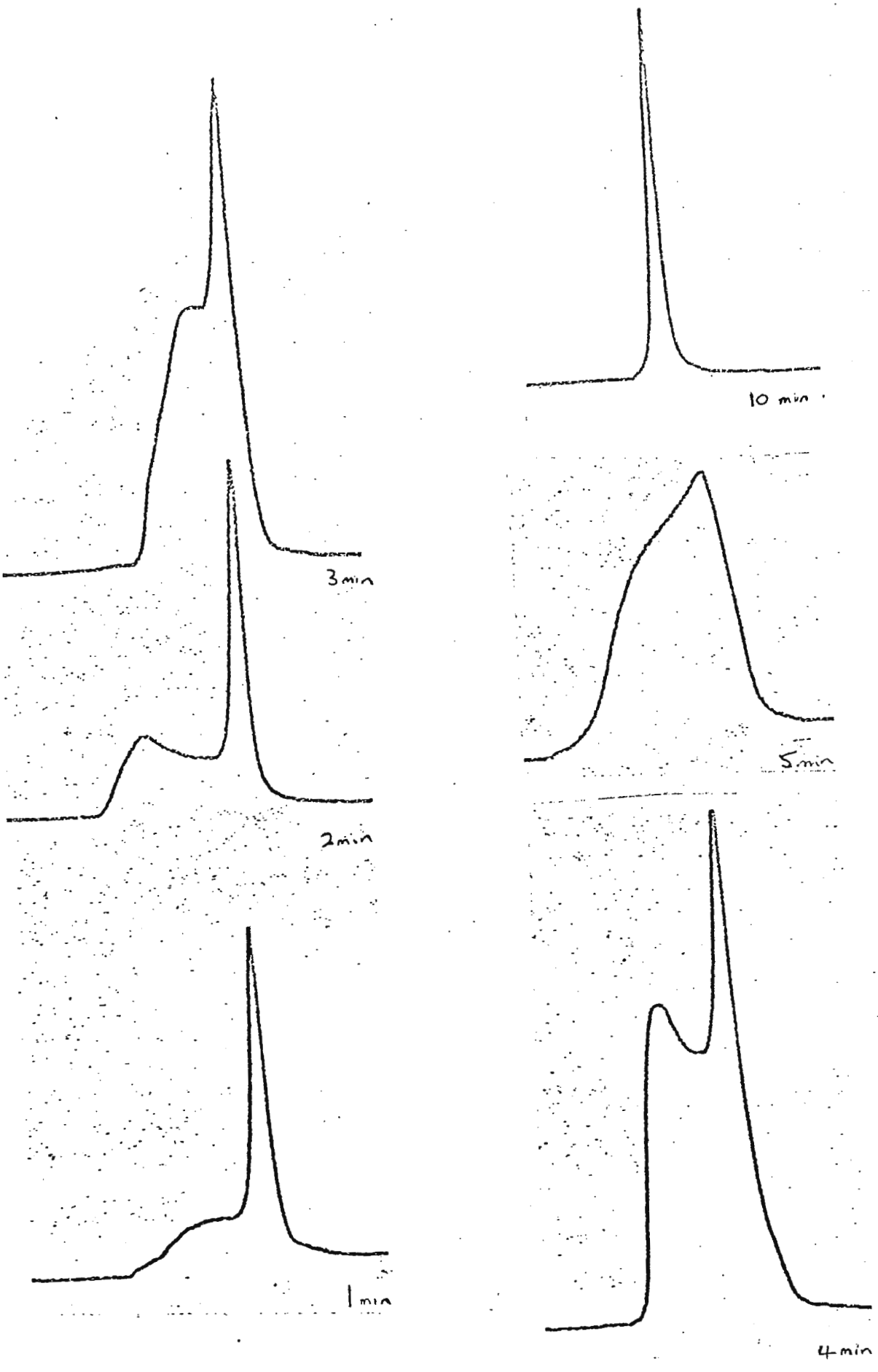
Concentration Gradients

When checking the structure of 2-(β amino ethyl) pyridine, we observed in CCl_4 solution on a Perkin Elmer R12 what we thought was an AB pattern for the NH_2 signal (2 strong centre lines with two outer weak lines which did not move when the spinning speed was changed). We thought this unusual and tried a second solution when we observed a different AB pattern which within 5 minutes had become a single line. We postulated an internal hydrogen bond and an exchange process but we were not able to observe the AB pattern again either by cooling to $-50^{\circ}C$ in $CDCl_3$ solution or by use of other solvents. What then is the explanation? One idea was that it was a concentration phenomenon due to layering of the solution in the preheater of the R12. To prove or disprove this, we made up a 2 layer solution in $CDCl_3$ (one layer dilute and the other concentrated) and observed the effect, at the layer interface, of spinning the sample over a period of time. (10 mins) using our pulsed Bruker HX90E. The results are shown in the accompanying figure where it can be seen that 2 signals can be observed for the NH_2 over the first five minutes of spinning and that eventually, at 10 minutes, only one signal is observed when complete mixing has occurred. We are not sure if this is the real explanation of our initial problem because we then have to assign the side peaks of the AB pattern to probable impurities. We would be interested to hear if any one else has observed similar concentration gradient effects.

Yours sincerely,

D Greatbanks R Pickford D Smith

B Wright D J McNeillie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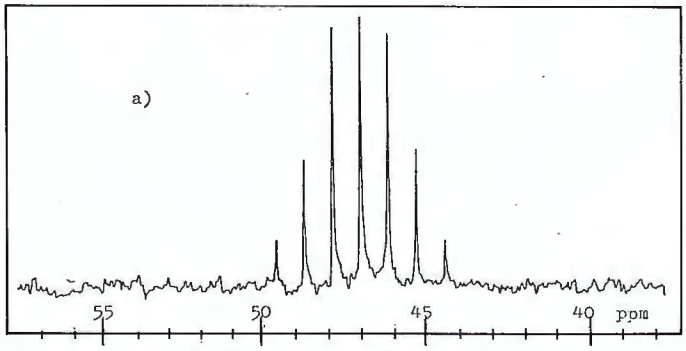
^{12}C Solvents Depleted Solvents: Deuterated Compounds

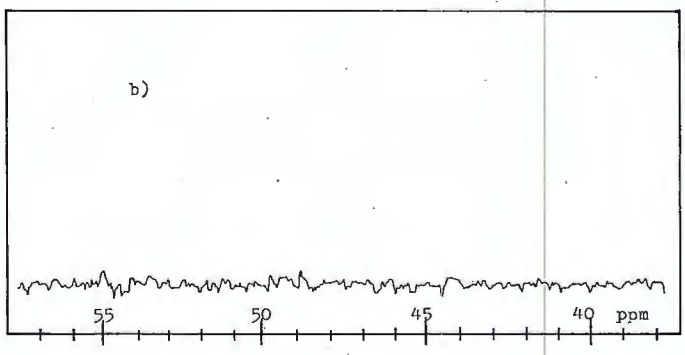
In Fourier transfer ^{13}C NMR spectroscopy, the signal-to-noise ratio, and thus spectrum quality, is often limited by the strongest signal. In a normal sample, there is much more of the solvent present than there is of the substance under test. For this reason, the solvent signal is frequently much stronger than the sample signal; thus the solvent tends to limit the sensitivity and usefulness of ^{13}C NMR measurements .

Fourier transform techniques increase the sensitivity of NMR spectroscopy to such an extent that the natural content of ^{13}C (1.1%) is often sufficient to provide ^{13}C solvent signals that mask the ^{13}C signals of the sample.

In order to minimize the solvent signal, E. Merck has developed a new class of Uvasols, in which the ^{13}C content is less than 10% of the natural level. These are compounds with ^{12}C content of from 99.93 to 99.95%. In addition, these Uvasols are synthesized with a deuteration degree of more than 99.5% in order to eliminate possible Overhauser amplifications in proton-noise de-coupled spectra which could increase solvent-signal amplitudes by a factor of as much as three and which, therefore, could mimic a higher level of ^{13}C than is actually present. Preparation techniques allow the synthesis of many different solvents. For example, chlorinated ^{12}C methanes (CCl_4, $CDCl_3$, CD_2Cl_2), ^{12}C methanol, and ^{12}C methyl halogenides, non proton solvents such as ^{12}C dimethylsulfoxide, ^{12}C dimethylformamide, ^{12}C tetramethyl urea, ^{12}C acetic acid and its derivatives and others in which the carbon atoms in a molecule have the same ^{12}C isotope content. At the present time, five ^{12}C solvents are commercially available from EM Laboratories.

Figure 1 compares the NMR spectrum of methanol with natural ^{13}C content (a) and the spectrum of methanol containing only 5% of the natural ^{13}C content (b). Both spectra were obtained under identical measuring conditions with a Varian XL-100 NMR spectrometer. Spectrum (a) shows the septet of the CD_3 group at 47.05 ppm with a ^{13}C-^{2}H spin coupling of 22 Hz in the region between 40 and 55 ppm relative to TMS. In spectrum (b), the same region is practically signal-free.





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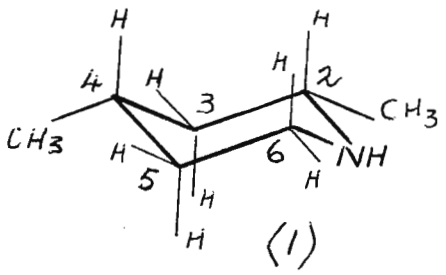
Nuclear Overhauser Enhancements and low-temperature T_1 Values in Noise Decoupled P.F.T. ^{13}C Spectroscopy

Our research programme involves the determination of conformational equilibria in interconverting cyclic compounds, using P.F.T. ^{13}C spectroscopy at reduced temperatures. This has led us to measure nuclear Overhauser enhancements and T_1 values in a model compound, cis-2,4 dimethylpiperidine (1).



(1)

Our J.E.O.L. PS100 spectrometer, fitted with ~~polar~~ pulse programmer and F.T. unit, is interfaced with a NICOLET 1085 20K computer.

The n.O. enhancements of TABLE I are for undegassed samples in $CDCl_3$, and were obtained from gated decoupling experiments. Values for the methyl carbons could not be separately assessed, owing to the closeness in chemical shift. In experiment A, the F.I.D. was transformed without enhancement of sensitivity (TC=0); in B, the same F.I.D. was given an exponential multiplication (TC=-3). Areas were obtained from computer print-out, using the Nicolet programme for absolute integrals, and also from measurements on expanded signals using a planimeter. The computer print-out of integrals was unreliable, often giving enhancements well in excess of the theoretical maximum (199%). Measurements using a planimeter were tedious but gave more reliable figures. The results justify our earlier mistrust of integral print-out, which led us to assess areas by measurement of steps in an integral plot, as in CW operation. In addition, the results suggest that carbons carrying the same number of protons give similar n.O. enhancements.

TABLE II summarises our results for T_1 values of carbons in (1), measured by the inversion-recovery method. The fall in T_1 values, as the temperature is lowered, confirms the high contribution of dipolar relaxation to T_1. Carbons carrying the same number of protons are seen to have

approximately the same T_1 values; more important, the T_1 values at -60° are very short compared with the pulse repetition time of 2 to 2.5s. which is normally used for a spectral width of 2500 Hz and 8K data points.

Summarising, in P.F.T. ^{13}C studies at temperatures below -50°, a comparison of integrals of carbons carrying the same number of protons should faithfully reflect the molecular proportions involved.

H. Booth
M.L. Jozefowicz

Department of Chemistry,
University of Nottingham.

TABLE I Nuclear Overhauser Enhancements in $^{13}C\{^1H\}$ P.F.T.N.M.R.

CARBON	nuclear Overhauser enhancements (% increase) via print-out		via planimeter	
	A	B	A	B
2	227	169	169	169
4	201	170	182	168
3	257	215	192	193
5	195	195	201	199
6	240	234	180	183
CH_3 (both)	202	174	177	160

Notes: spectral width 2500 Hz; pulse width 4.0 μs (40°).
data points 8192; repetition time 30s.

TABLE II ^{13}C Relaxation Times (T_1) (s)

Temperature	+21°	-40°	-60°
CARBON			
2	4.4	1.1	0.43
4	5.1	1.2	0.43
3	2.8	0.75	0.26
5	2.8	0.80	0.29
6	2.5	0.74	0.26
CH_3(a)	2.7	0.79	0.32
CH_3(b)	2.7	0.81	0.32

Notes: solvent $CDCl_3$ (undegassed); spectral width 2500Hz; data points 8192; repetition time 30s.

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DEPARTMENT OF CHEMISTRY DAVIS, CALIFORNIA 95616

October 14, 1974

Professor Barry Shapiro
TAMU NMR
College of Science
Texas A & M University
College Station, Texas 77843

Title: Proton T_1's in Paramagnetic Molecules

Dear Barry:

My apologies for provoking both a blue and pink slip, but installation and trouble-shooting of our FTNMR system has caused me to miss more than one deadline.

During this past year we have become interested in the use of relaxation data for determining the structure of dimerized porphyrins. Recent linewidth studies of dicyanohemin in methanol-d_4 revealed[1] that certain hemin methyl proton signals were selectively relaxed at high concentrations, suggesting intermolecular dipolar relaxation within the dimer.

With the installation of our FTNMR system, (JEOL PS-100/DIGILAB NMR-3), we have extended our studies to T_1 data. T_1's in this system are very short, (< 100 m sec), and therefore posed some difficulty originally, since the timing-jitter on a disc-collect yielded an ill-defined τ value in the 1-100 m sec range. Correction of this problem by incorporating the ability to perform in-core collects up to 16K points has yielded useful data which confirms our previous linewidth studies.

The lesson we learned from this foray into short T_1 measurements (paramagnetic systems, quadrupolar nuclei, i.e., Br^{79}) is that, not only must the τ value (teletyped-in) be calibrated on a scope, but the values must be checked over a sufficiently long time to detect any scatter. Typical T_1 data for our sample are given in the figure.

Sincerely yours,

Gerd

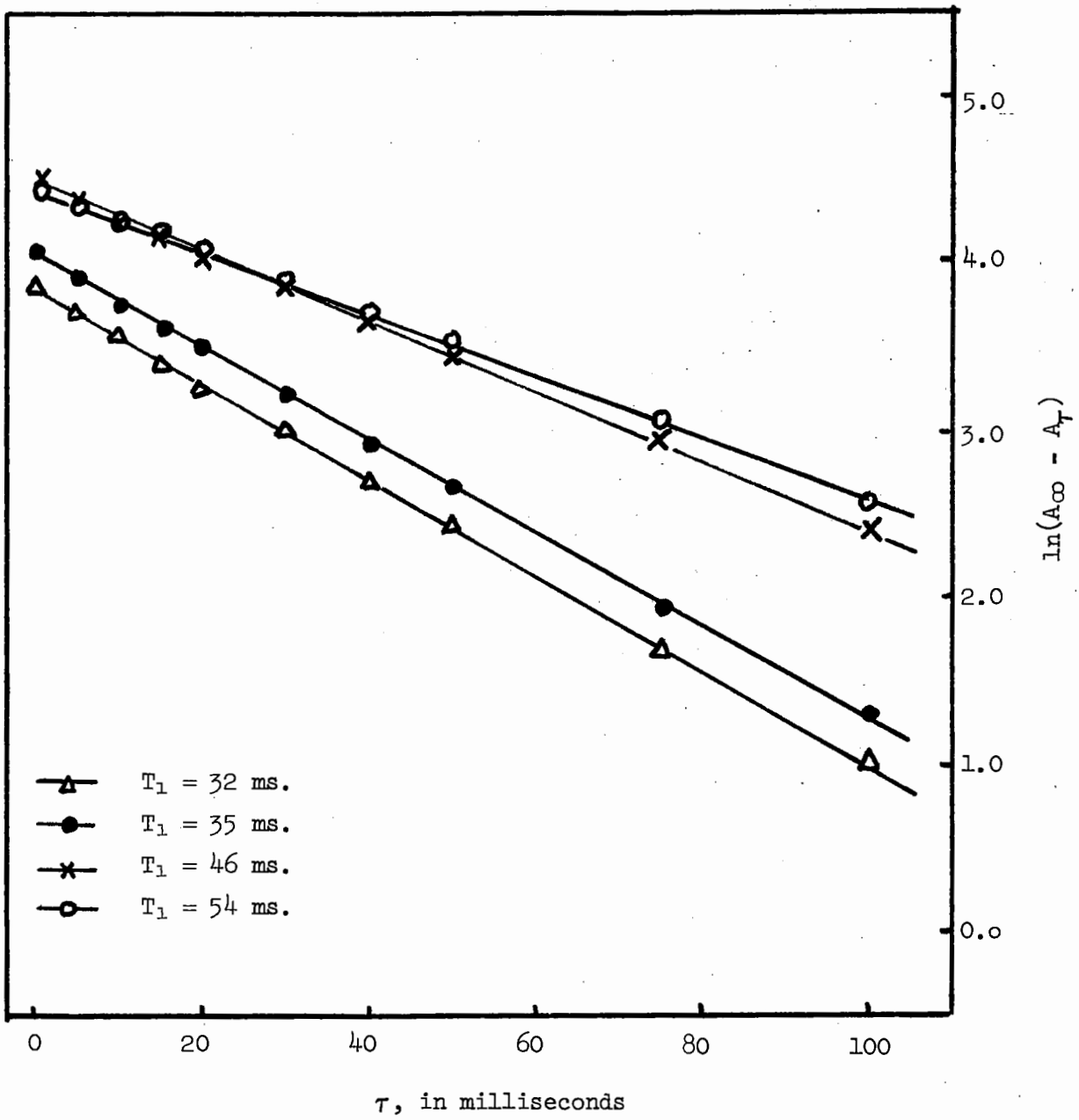
Gerd N. La Mar
Professor of Chemistry

GNL/ds

(1) G. N. La Mar and D. B. Viscio, J. Amer. Chem. Soc. (in press).

Dicyano Hemin Methyl Proton T_1's By 180°-τ-90° Pulse Sequence

(Methanol-d_4, at -76°)



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October 15, 1974

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

SPIN LATTICE RELAXATION MEASUREMENTS USING RAPID SCAN FT-NMR

In this communication we describe a new approach for convenient measurement of T_1's using the rapid scan FT-NMR (1,2). In this method, which is in some ways analogous to the saturation-recovery (90°, τ, 90°) pulse method (3,4), we establish the initial state of the spin system by applying a saturating rf field, H_2, to the spectral lines to be studied. Ideally such an rf field should cause complete demagnetization in a time of the order of a few times the relaxation time. H_2 is then switched off and after a variable delay time τ the spectrum is rapidly scanned under fast passage conditions with an rf field, H_1, of appropriate strength. The fast passage response thus obtained is cross correlated or treated with an analytical function to yield a partially relaxed slow passage spectrum. Repetition of the saturation and observation sequence permits the determination of T_1 for each saturated line from its exponential recovery.

In practice we found it difficult to achieve complete demagnetization of the sample with the rf fields available on the Varian HR-220 instrument. Although the longitudinal component of magnetization was vanishingly small, a signal was invariably present on turning off the saturating rf field due to residual transverse component of magnetization. To obtain a well-defined demagnetized initial state, therefore, this signal was destroyed by temporarily inhomogeneizing the H_0 for ~10 msec. (4) after turning H_2 off.

We give an example of the use of this method in Figure 1. The slope of the straight line plot of ln $(S_\infty - S_\tau)$ vs τ yielded $T_1 = 9.3 \pm 0.5$ sec, in good agreement with the value of 9.5 sec obtained from a 180°, τ, 90° pulse FT study of the same sample. Saturation need not be limited to one line, although this method is not expected to give correct T_1's in a coupled spin system (5). Two or more audio oscillators can be used

Professor Shapiro October 15, 1974

to selectively irradiate lines, or a noise modulated H_2 can be employed to saturate lines in one region of a spectrum. An advantage of the rapid scan saturation technique over the 180°, τ, 90° pulse method is that it requires only about 5 times the relaxation time in the presence of the rf field, and not $5T_1$, for establishment of the initial state of the spin system. In several situations, the relaxation time may be significantly shorter than T_1 resulting in considerable saving of time.

Sincerely yours,

Raj K. Gupta
The Institute for Cancer Research
Philadelphia, Pennsylvania 19111

James A. Ferretti

Edwin D. Becker
National Institutes of Health
Bethesda, Maryland 20014

REFERENCES

1. R. K. Gupta, J. A. Ferretti, and E. D. Becker, J. Magn. Resonance 13, 275 (1974).

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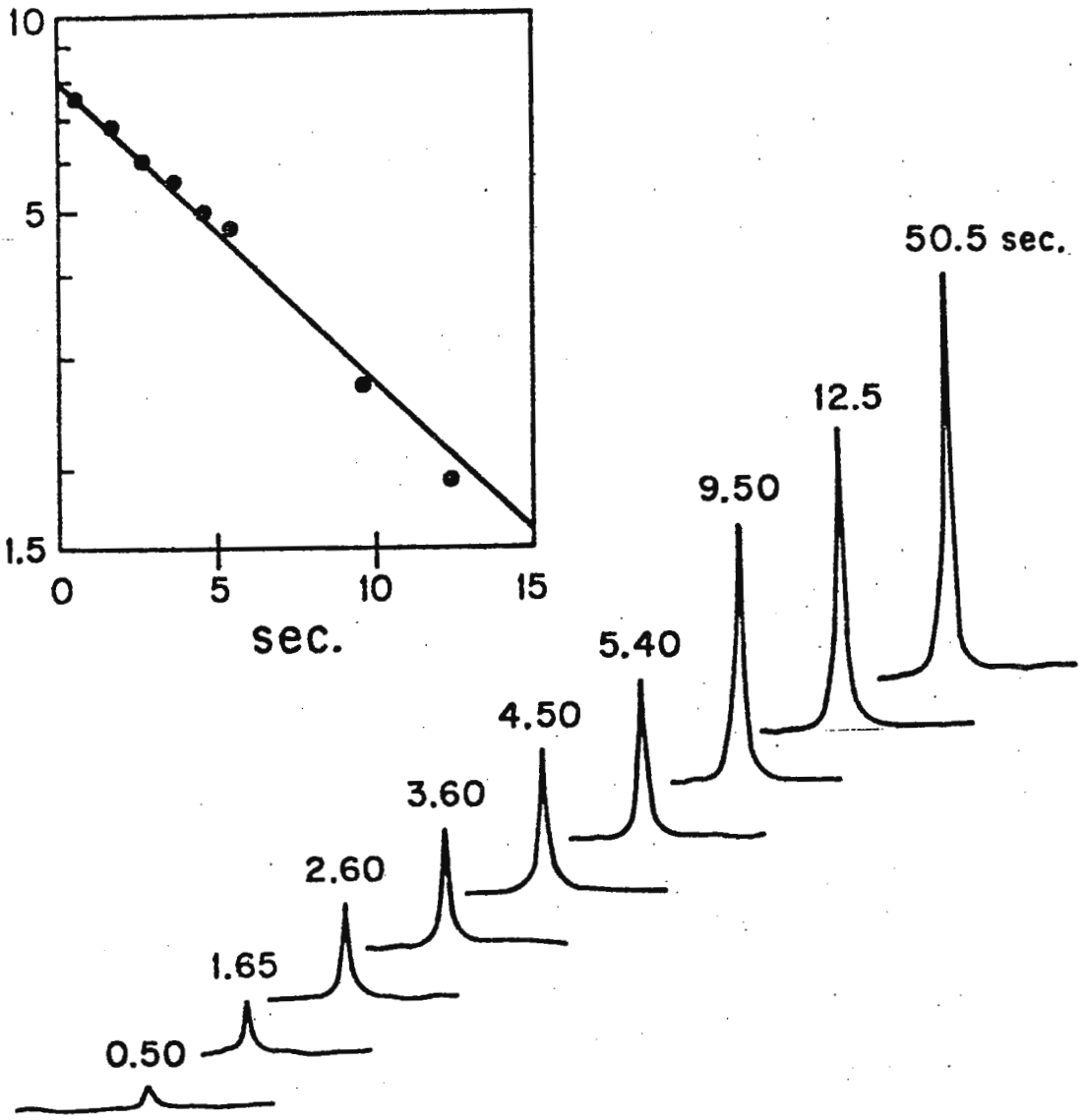


Fig. 1 - Partially relaxed proton spectra of 1% TMS in $CDCl_3$ obtained on the Varian HR-220 spectrometer using Rapid Scan FT NMR. The times indicated are the intervals between turning off H_2 and passage through the resonance. The scan rate was 200 Hz/sec; the rf power, H_1, corresponds to a flip angle of about 30°. Data were analyzed with the theoretical function (1) and an exponential filter of 2 Hz. The insert shows the semilog plot of the T_1 measurement.

UNIVERSITY of PENNSYLVANIA
PHILADELPHIA 19104

The School of Medicine
JOHNSON RESEARCH FOUNDATION
DEPARTMENT OF
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

October 15, 1974

Dr. Bernard L. Shapiro
Dept. of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

The sample temperature control system on the HR-220, as supplied by the manufacturer is rather unsatisfactory. Most of the difficulties arise from the rather long time constant, approximately five minutes, for equilibration of the probe to a new temperature. Since the temperature dial seems to rapidly loose its calibration one must resort to a hunt and seek routine involving iterations around the desired setting. This process can easily consume several hours.

These difficulties have been obviated by making a new heater sensor tube with an extra port into which is inserted a thermistor. In this way one can directly measure the carrier gas temperature after it has swept by the heater-sensor. There is a thermal gradient between the thermistor and the sample region of the probe. However, a simple calibration suffices to relate the probe sample temperature to the thermometer reading. It is convenient to moniter the probe's approach to thermal equilibrium with another thermistor inserted in place of the sample, recording the temperature on a strip chart recorder. It is with the second thermistor that the calibration curve was made. The purpose of the first thermistor thermometer is to allow one to correctly set the controller without having to wait for thermal equilibrium.

Dr. Bernard L. Shapiro

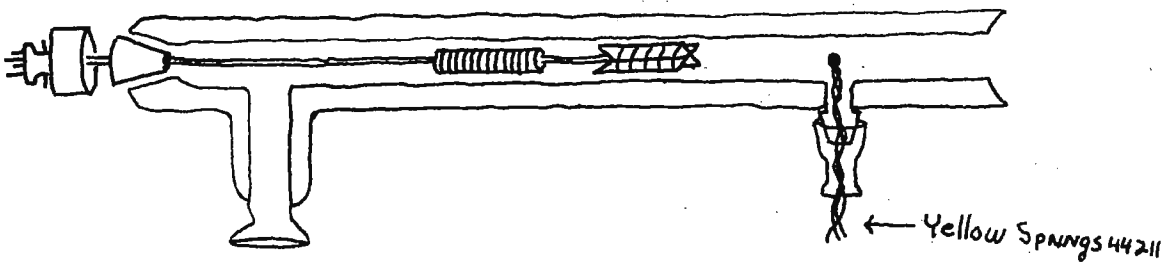
October 15, 1974

The magnet of this HR-220 has been fitted with an automatic liquid nitrogen filling device. Since a source of liquid nitrogen is continuously available, I derive the carrier gas for the temperature controller directly from the liquid nitrogen line, whence it is delivered to a small tank, 5 cm. diam. and 25 cm. long, outfitted with a pressure regulator. At the usual rate of consumption, 15 CFH, the liquid nitrogen vaporizes completely in the deliverly tube before it gets to the expansion tank. The gas is at room temperature by the time it arrives at the temperature controller. This set up assures a continuous, clean source of N_2 gas which is cheaper than water pumped nitrogen delivered in tanks.

Sincerely,

George G. McDonald

George G. McDonald



P. S.

Please credit this letter to the account of Dr. Mildred Cohn.

ENC Inc. Sixteenth Experimental Nuclear Magnetic Resonance Spectroscopy Conference

Asilomar, California, April 20-24, 1975

October 18, 1974

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

This is a preliminary announcement for the forthcoming ENC. We plan on invited sessions on the following topics: biological molecules, polymers, shift reagents, paramagnetic samples, experimental aspects of C^{13}, other nuclei, solids surfaces and wide line, relaxation, spin polarization, new experimental techniques and new digital techniques.

Although there will only be a limited time available, readers who have possible contributed papers are encouraged to submit abstracts to me and I shall forward them to the appropriate session chairman for consideration either in his session or in the poster session.

We look forward to a good ENC and hope many of the TAMU NMR Newsletter readers can attend.

Sincerely yours,

Jerry Swalen

J. D. Swalen

/jmv

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October 21, 1974.

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas
U.S.A. 77843

Dear Professor Shapiro:

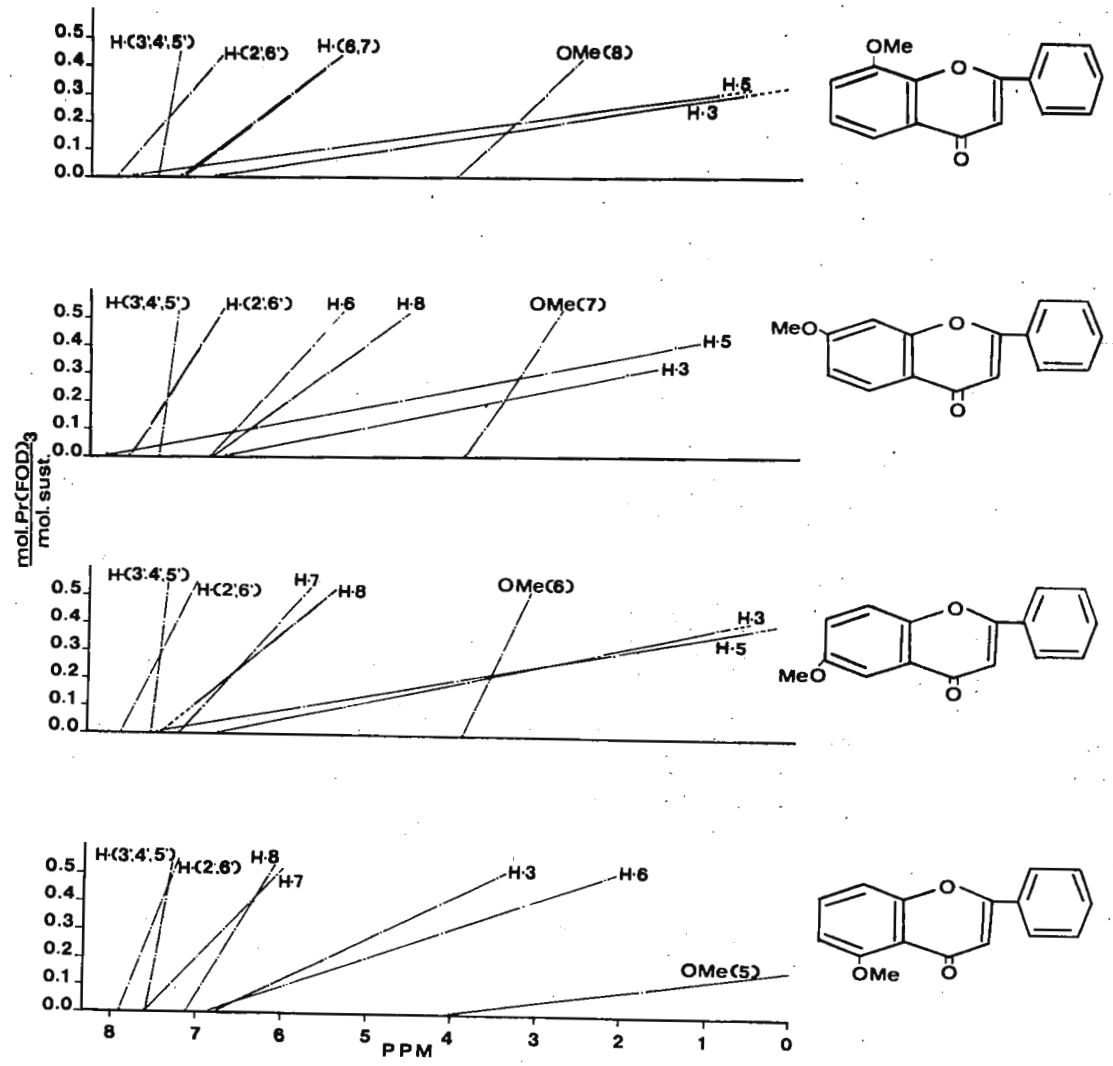
Shift Reagent Behavior of Some Flavones:

A paper reporting the C-13 assignments of flavone, for which it was necessary to synthesize 5,6,7,8-tetradeuteroflavone, 2',3',4',5',6'-pentadeuteroflavone and 4'-bromoflavone, was presented at the 167th ACS National Meeting (Los Angeles) and will appear in a forthcoming issue of J. Magn. Resonance. All proton parameters of flavone, which were refined by LAOCOON III calculations, are also described therein, as is the behavior of the compounds with $Pr(fod)_3$, which turned out to be the most useful shift reagent for these substances. Some preprints are available.

Since then, we started to synthesize the eight possible monomethoxyflavones, in order to study them with $Pr(fod)_3$. The work on the A-ring substituted compounds has been completed and is summarized in the figure.

Two papers describing flavones in the presence of europium shift reagents came to our attention (1,2). Several general rules to predict shift reagent behavior and to elucidate flavone structures are given there, although only flavones having always a 5-MeO group were examined. It was stated for instance that H-6 shows larger shift values than H-8. This is true for 5-methoxyflavone, is not valid in 7-methoxyflavone and can obviously not been tested in 6- or in 8-methoxyflavone. Furthermore in fla-- vone itself, in the pentadeuterated analog and in 4'-bromoflavone, H-8 shifts more than H-6. Since from our own work in shift reagent studies with aromatic substrates (3) we know that the behavior of $Pr(fod)_3$ is similar to that of $Eu(fod)_3$ except mainly the direction of the shifts, other reasons should account for the experimental results obtained with 5-methoxyflavone in comparison to the remaining flavones.

(1).- M. Okigawa, N. Kawano, W. Rahman and M. M. Dhar, Tetrahedron Letters, 4125 (1972).
(2).- M. Okigawa and H. Kawano, Chem. and Ind., 850 (1973).
(3).- P. Joseph-Nathan and V. M. Rodríguez, Rev. Latinoamer. Quím., 5, 12 (1974).
(4).- M. R. Willcott, R. E. Lenkinski and R. E. Davis, J. Amer. Chem. Soc., 94, 1742 (1972). We are indebted to Prof. Davis for a copy of the program.



After some calculations using the PDIGM program (4), it was evident that in 5-methoxyflavone the lanthanide atom is interacting simultaneously with the carbonyl and the methoxyl oxygens as a bidentate ligand, while in the remaining compounds the interaction occurs escentially at the C=O. The change in the association position is therefore responsible for the variation of the relative shifts that are induced on the various protons.

The synthetic work was performed with the assistance of Ma. C. Hernández, an undergraduate student.

Sincerely yours,

Dr. Pedro Joseph-Nathan
Professor of Chemistry

José G. Mares, B.Sc.
Graduate Student

PJN/psp

194-19

DEPARTMENT OF THE NAVY
NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:
6052/DWM:dgg
29 October 1974

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry,

Last month I mentioned briefly the interesting ^{13}C relaxation time data we were finding in our studies of hydrocarbon gels. Now we have completed a proper series of pulsed inversion-recovery FT measurements of poly(1-decene) in benzene, and the results are worth communicating - even though our ten months aren't up yet.

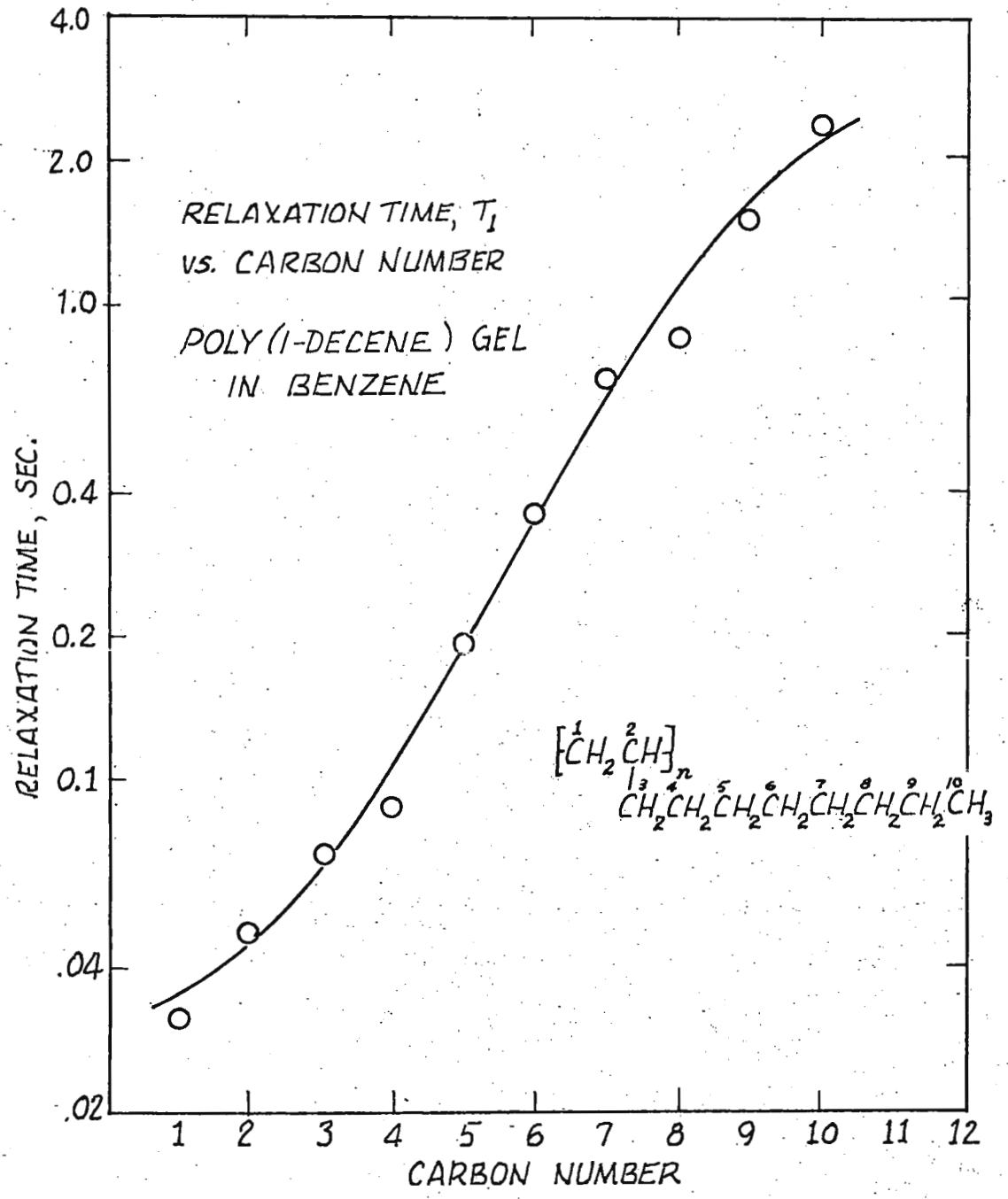
The poly-olefins we are studying are simply polyethylene with alkyl side-chains on every other carbon. Poly(1-decene) has octyl groups as its branches, and these render the polymer soluble in most hydrocarbons with the formation of viscous gels. A 20% (w/v) benzene solution of poly(1-decene) is stiff and rubbery, yet it gives a quite decent ^{13}C nmr spectrum (25.14 MHz) in which we observe the increase of line-width from outer to inner carbons of the alkyl group. This was - without further proof - attributed to decreasing spin-lattice relaxation times, since the correlation times of segmental chain motions could be reasonably expected to increase from the free end to the bound end of the branch.

The enclosed plot shows what we observed in the PRFT series. It appears that segmental motions of the polyethylene backbone set a lower limit for T_1 at around 30 msec, while the terminal methyl exhibits a fairly ordinary 2.3 sec T_1. In between, the values vary as shown in the plot. The shape of this line appears vaguely sigmoidal, as might be guessed from the boundary conditions. At any rate, it is a gratifying demonstration of what we expected to find, and bears out Levy and Nelson's prescient comment in "^{13}C NMR for Organic Chemists" (p. 190) that using this new approach, "Spectroscopists ... will undoubtedly learn much about motions along polymer chains and in side groups."

Best regards,

Don

Donald W. Moore


RELAXATION TIME, T_1
vs. CARBON NUMBER
POLY (1-DECENE) GEL
IN BENZENE
RELAXATION TIME, SEC.
4.0
2.0
1.0
0.4
0.2
0.1
.04
.02
1 2 3 4 5 6 7 8 9 10 11 12
CARBON NUMBER
$[CH_2\overset{2}{C}H]_n$
$\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}H_3$

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- Failsafe

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

October 22, 1974

Building 2, Room B2-08

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

Title: pH Titration Curves of Histidine Protons in Metmyoglobins

We have recently reported (1) on the observation of titration curves of the histidine C-2 protons in human metmyoglobin (Fig 1). This extends the earlier studies with the homologous sperm whale and horse metmyoglobins(2). In addition, we have studied the effects of the active site ligand, sodium azide, on the pH titration curves of the three proteins. (Figure 2 shows the pattern for human metmyoglobin.)

In the absence of azide, all three metmyoglobins have two unusual titrating resonances. One, curve 4, (Fig 1), exhibits a low pK and a second inflection at high pH. The second, curve 3, has a high pk and is shifted to higher field than normally found for a histidine C-2 proton. In all three cases, five of the histidine C-2 protons from the normal complement of histidines (Sperm whale, 12; horse, 11; and human, 9) are not observed.

In the presence of excess azide ion, all three homologous proteins behaved in the same way. Azide ion causes; a) a shift of the high pK curve 4 to high field; b) a shift of the low pK curve 3 to lower field and abolition of the second inflection; c) the appearance of two new titrating resonances (curves 5 and 6).

We are preparing a manuscript in which we discuss possible assignments of these resonances and the processes which contribute to these observations.

Yours truly,

Melvin B. Hayes
Reproduction Research Branch
National Institute of Child
Health and Human Development

MBH:ell

Please credit this to the account of Jack Cohen.

References

1) Melvin B. Hayes, Jack S. Cohen, and Hanspaul Hagenmaier, Abstracts of The Biochemistry/Biophysics 1974 meeting, June 1974, number 1574.

2) J. S. Cohen, H. Hagenmaier, H. Pollard, and A. N. Schechter, J. Mol. Biol. (1972), 71, 513-519.

cor

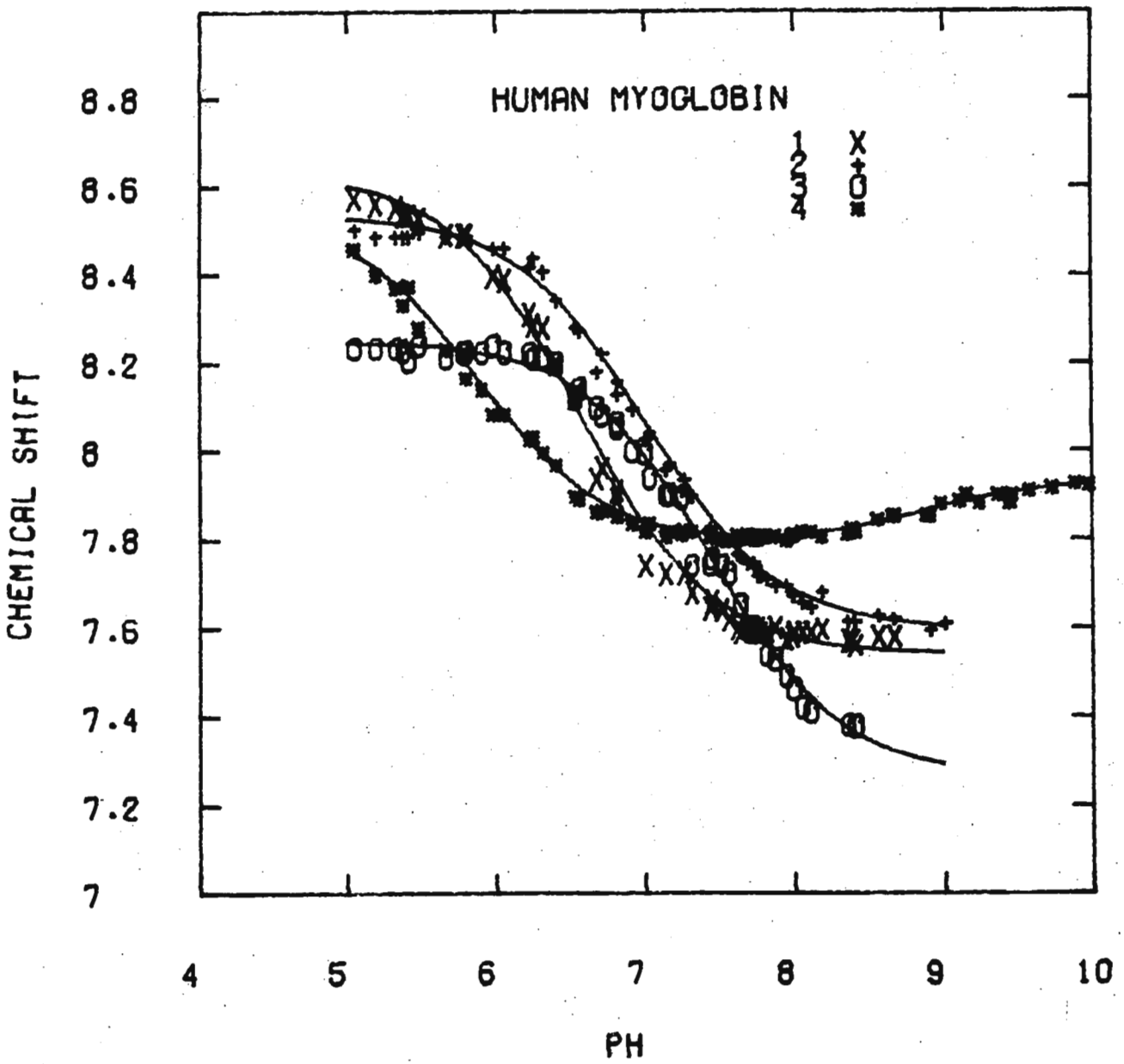


Figure 1. pH titration curves of histidine C-2 protons in human metmyoglobin.

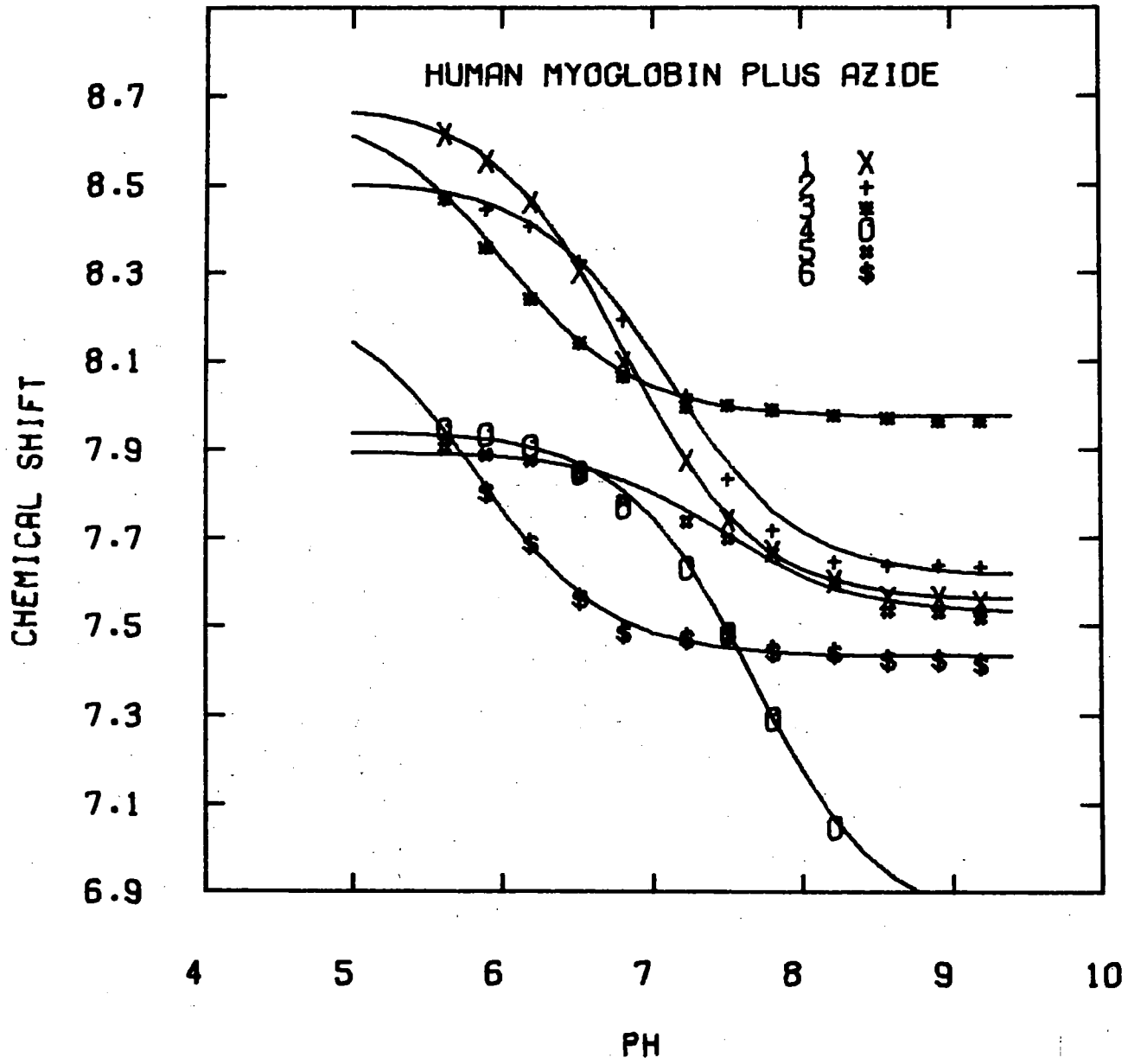
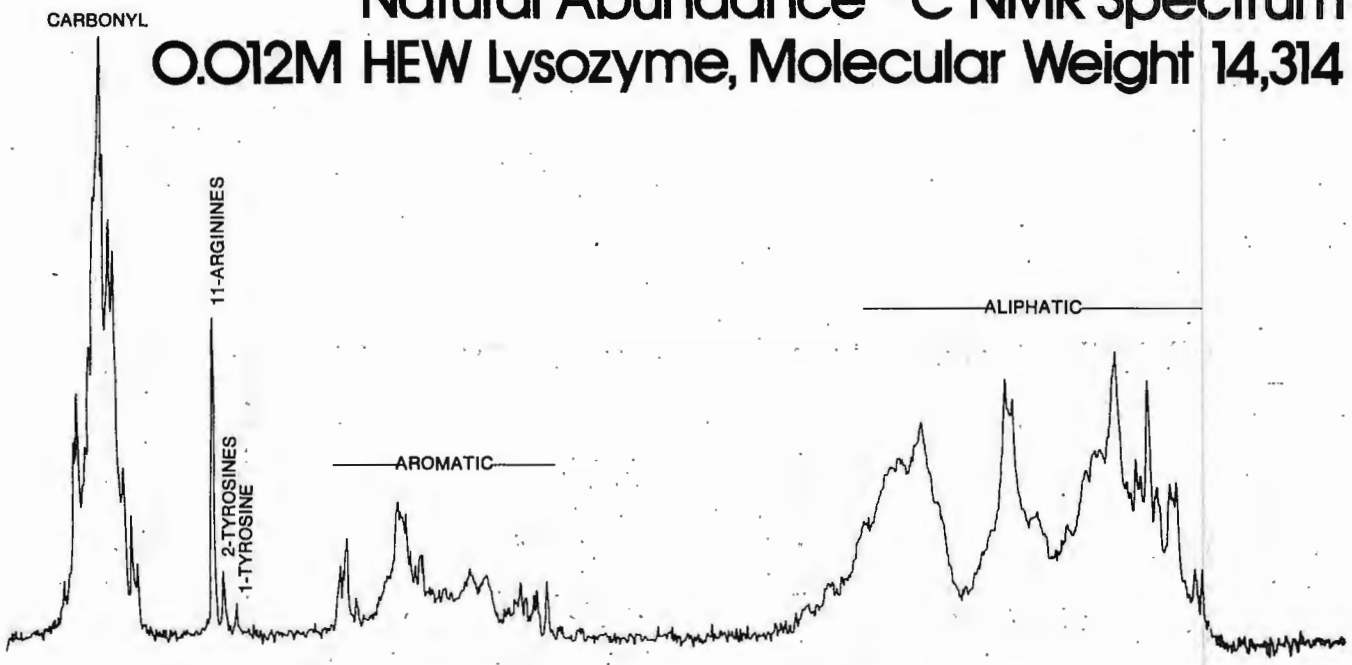


Figure 2. pH titration curves of human metmyoglobin in the presence of excess sodium azide.

Natural Abundance ^{13}C NMR Spectrum
O.012M HEW Lysozyme, Molecular Weight 14,314



Proton-decoupled natural abundance ^{13}C spectrum of hen egg white lysozyme in 0.15M NaCl in 9:1 H_2O/D_2O, pH 4.0, 45°C. Recorded with a TT-14 system[1] at 15.08 MHz using a 20 mm sample tube; 37,107 90° pulses; 4096 time-domain points; and 1.165 Hz digital line broadening. This spectrum demonstrates that in a small protein, single carbon resonances such as the one assigned above to C^{ϵ} in a single tyrosine residue, can be observed after only five hours of signal averaging with use of the 20 mm sample technology developed at Indiana University by Dr. Adam Allerhand.[2,3]

1. Sample run at the University of Chicago, courtesy of Dr. Philip Keim, Pritzker School of Medicine.
2. A. Allerhand, R.F. Childers, E. Oldfield, J. Magn. Resonance, *11*, 272 (1973).
3. E. Oldfield and A. Allerhand, Proc. Nat. Acad. Sci. USA, *70*, 3531 (1973).

HIGH SENSITIVITY CARBON-13 FT-NMR
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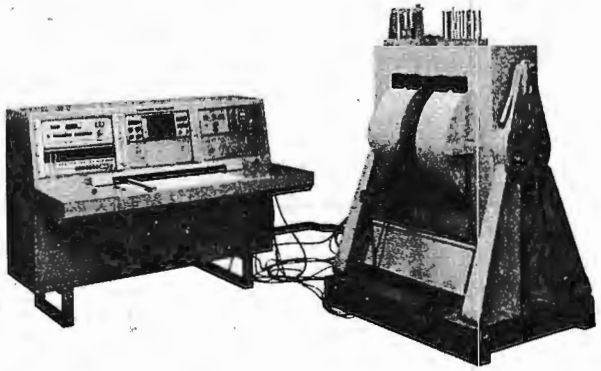

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23rd October, 1974

NOTATION FOR COUPLING CONSTANTS

Dear Barry,

There appears to be no accepted ordering for the nuclei when a coupling constant is specified. Thus one finds in the literature both J_{PH} and J_{HP}, sometimes in the same paper. However, a consistent ordering would appear to be desirable. We would therefore like to propose that the heavier nucleus is placed first, e.g. J_{PH} is used rather than J_{HP}. This has the desirable result that J_{CH}, which seems to be almost universally used, conforms to the notation.

Furthermore, when a coupling path is given for a homonuclear interaction, one can use the order which gives the heavier second nucleus, e.g. J_{HNCH} rather than J_{HCNH}. Obviously the principle can be readily extended. Incidentally, we find designation of the coupling path to be very useful, and we hope that authors would indicate the path more often.

We have found these ideas very useful in sub-dividing the chapter on Coupling Constants in the Chemical Society's Specialist Periodical Reports on NMR, Volume 4 (in press).

It might also happen to be desirable on occasion to indicate which nucleus had its spectrum taken to obtain the coupling constant. This can be done by using an atomic symbol in bold lettering. Thus $^{1}J_{\mathbf{C}H}$ would indicate the ^{13}C spectrum was observed, whereas $^{1}J_{C\mathbf{H}}$ would indicate the ^{1}H spectrum was used. We are indebted to Dr. B. J. Kimber for this last suggestion.

We would be interested in any comments on these suggestions,

With best wishes,

Robin Harris

Dr. R. K. Harris

R. Grinter

Dr. R. Grinter

Professor B. L. Shapiro
Department of Chemistry,
Texas A and M University,
College Station, Texas 77843
U.S.A

RH/RG/KJS

194-27

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PRINCIPAL Sir Harry W. Melville, K.C.B., F.R.S.
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LONDON E1 4NS
Tel. 01-980 4811

Dr. B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, TX 77843,
U.S.A.

28th October, 1974

Dear Barry,

International Meeting on N.m.r., St. Andrews, 6-11th July, 1975

The meeting will deal with selected topics in high resolution NMR Spectroscopy and will comprise six consecutive symposia.

Symposium 1.	RECENT APPLICATIONS OF ^{13}C AND OTHER NUCLEI STUDIES TO CHEMICAL PROBLEMS
Chairman:	Dr. R.K. Harris
Plenaries:	Professor A.R. Battersby
	Professor E. Lippmaa
Symposium 2.	NMR STUDIES OF ORIENTED MOLECULES
Chairman:	Dr. J.W. Emsley
Plenary:	Professor P. Diehl
Symposium 3.	NMR STUDIES OF SOLIDS
Chairman:	Dr. N. Boden
Plenary:	Professor J.S. Waugh
Symposium 4.	CORRELATION AND FOURIER SPECTROSCOPY
Chairman:	Dr. R. Freeman
Plenary:	Dr. D. Ziessow
Symposium 5.	APPLICATIONS OF NMR TO BIOLOGICAL SYSTEMS
Chairman:	Dr. J. Feeney
Plenaries:	Dr. M. Bradbury
	Dr. R. Dwek
Symposium 6.	THEORETICAL ASPECTS OF NMR
Chairman:	Dr. C.W. Haigh
Plenary:	Professor P.D. Ellis

Contributed Papers

In addition to the Plenary and Invited Lectures, there will be a limited number of short contributed papers included in the programme and probably a poster session also. Anyone wishing to contribute a paper should submit, not later than 1 FEBRUARY 1975, a title and synopsis (ca. 250 words).

Accommodation

Accommodation for registered participants will be available in University Hall, St. Andrews, which is adjacent to the Chemistry Department (where the symposia will be held).

Fees

The registration fee (including VAT) will be of the order of £17.50, and the accommodation charge of the order of £20.00.

Full Details

From: Dr. J.F. Gibson, The Chemical Society, Burlington House, London, W1V OBN

With best regards,

Ed

Professor E.W. Randall.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-559122
TELEX 47661

29th October, 1974

Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843,
U.S.A.

Dear Barry,

title: Vibrational Averaging of Dipolar Couplings

Our new XL-100 spectrometer has arrived and is now producing some beautiful spectra of oriented samples. Pulse spectrometers are a great inovation for studying the spectra of oriented molecules, but more of the experimental aspects in my next contribution. At the moment I would like to make a plea that in using the results of the NMR spectroscopy of oriented molecules to derive molecular properties it should be obligatory to allow for averaging of dipolar couplings over vibrational motion. The implications for molecular shape are obvious; in some cases the effect is small and it is tempting to assume that for, say, inter-proton dipolar coupling in planar systems there is no need to go through the process of vibrational averaging. But this is not always true and since calculation of an "effective structure" as proposed by Nigel Lucas (1-3) can be made routine (almost), we always now go through this procedure. To date we have carried out about twenty calculations of the effects of vibrations with some interesting results. The essential step in the process is of course calculation of the matrix L connecting normal coordinates with cartesian displacements, and we use for this the excellent program SOTON VIB (4), written by the vibrational spectroscopy group in Southampton. This program has many advantages over similar routines, but also has the advantage of outputing the L matrix desired.

It should be remembered that if S matrix elements are required then vibrational averaging can have a large effect, even when molecular shape is unaffected. This is always true, if at least one of the interacting nuclei is a proton, but not, in our experience, if only heavier nuclei such as carbon and fluorine are involved.

Professor B. L. Shapiro 29th October, 1974

Very briefly, topics investigated so far have included the effects of vibrational averaging on rigid molecules showing shape anomalies (such as cyclobutadiene iron tricarbonyl), deuterium isotope effects, and molecules having internal rotors. The latter have yielded some particularly interesting results, some of which will be appearing in print quite soon.

The vibrational work has been done in collaboration with my colleagues John Lindon, and Dave Stephenson and owes a great deal to their programing skill.

Best wishes,

Jim Emsley

J. W. Emsley

1. N. J. D. Lucas, Mol. Phys., 22, 147 (1971).

2. N. J. D. Lucas, Mol. Phys., 22, 233 (1971).

3. N. J. D. Lucas, Mol. Phys., 23, 825 (1972).

4. I. R. Beattie, N. Cheetham, M. Gardner and D. E. Rogers, J. Chem. Soc. A, 2240 (1971).

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

31 October, 1974

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843 USA

Adjustable Relaxation Time: FT-ICR

Dear Barry,

Many of your readers are aware of the many superficial similarities between NMR and ion cyclotron resonance (ICR) spectroscopy: coherent motion excited by an r.f. source, double-resonance and saturation experiments to detect magnetic or kinetic coupling, and the feasibility of obtaining a spectrum by Fourier transformation (FT) of the transient response to a brief excitation[1] rather than by conventional scanning of the steady-state response to a continuous excitation. FT-methods provide ICR spectra about 10,000 times faster than with continuous-wave (CW) scanning, compared to a speed advantage of about a factor of 1,000 for FT-NMR of carbon-13.

However, a fundamental difference between NMR and ICR is that for NMR, relaxation is generally determined by intra-molecular interactions (e.g., dipolar coupling), while in ICR, relaxation is determined by inter-molecular collisions. Thus it is possible to make ICR relaxation times arbitrarily long by diluting the sample (reducing the pressure), to provide arbitrarily high resolution spectra, with the use of signal-averaging of the transient ICR signals from successive excitations.

As with NMR, ICR may be carried out by either frequency- or magnetic field-sweep mode; all present conventional ICR instruments use field-sweep, where the field must be swept over a range of several kilogauss, with concomitantly poor field homogeneity and poor spectral resolution. The FT-ICR experiment is conducted at constant magnetic field, and thus permits much higher field homogeneity and better resolution. Finally, the ICR cyclotron motion itself has the effect of "spinning the sample", with further reduction in field inhomogeneity and even better spectral resolution than the resolution of the magnetic field. [Such averaging is less effective in conventional ICR, because the ion path is cycloidal or spiral, rather than circular, during the observation period.]

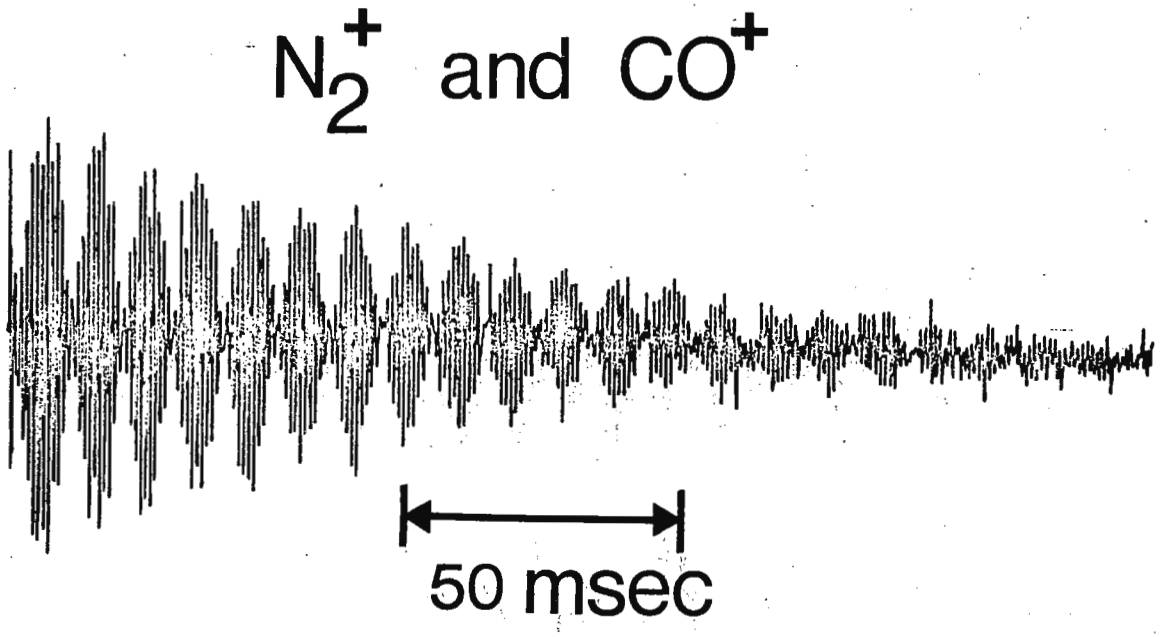
In conclusion, Fourier methods can do little to improve NMR resolution, but have improved ICR spectral resolution by orders of magnitude, by simultaneous introduction of signal-averaging, frequency-sweep rather than field-sweep, and "spinning the sample"! By combining this high mass resolution with the inherent high sensitivity of ICR, FT-ICR promises to open up a whole new field of mass spectroscopy of micro-quantities of low-volatility compounds of organic or biological interest, such as polypeptides, carbohydrates, nucleotides, antibiotics, and other natural products.

Sincerely,

Melvin B. Comisarow and Alan G. Marshall*

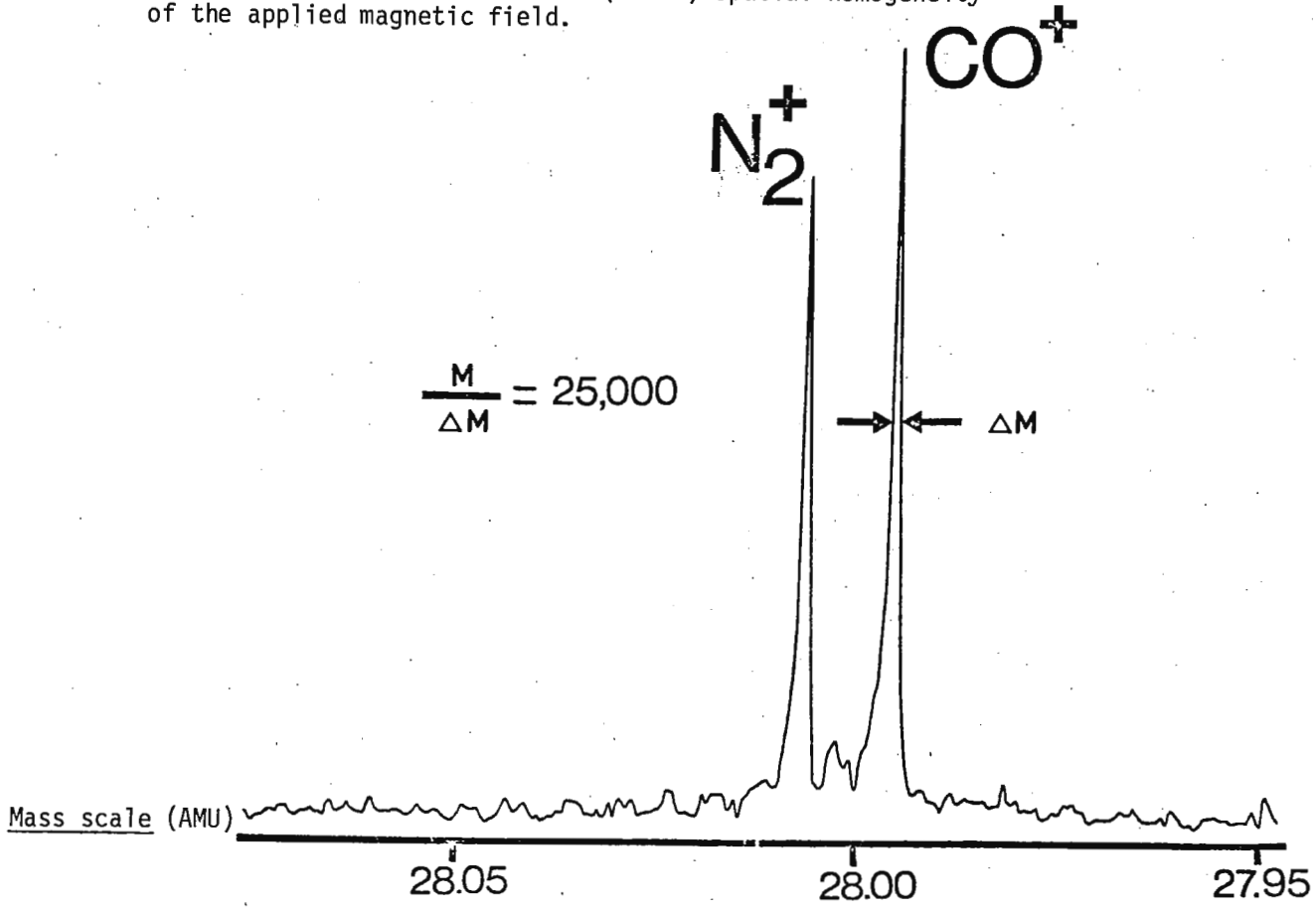
*to whose TAMU account this contribution should be credited.

1. M. B. Comisarow and A. G. Marshall, Chem. Phys. Lett. 25, 282 (1974);
M. B. Comisarow and A. G. Marshall, Chem. Phys. Lett. 26, 489 (1974);
M. B. Comisarow and A. G. Marshall, Can. J. Chem. 52, 1997 (1974);
M. B. Comisarow and A. G. Marshall, J. Chem. Phys., in press.



Top: ICR transient signal for an approximately equimolar mixture of N_2 and CO, ionized by electron impact.

Bottom: Fourier transform of the above ICR transient to give a frequency spectrum, where the ion cyclotron frequencies are related to ion mass as shown on the horizontal scale. As discussed in the text, the resolution seen here is about ten times better than the (known) spatial homogeneity of the applied magnetic field.



TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

November 4, 1974

Dr. Bernard L. Shapiro
TAMU - Department of Chemistry
Campus

Title: ^{13}C NMR of Alkylammonium Carboxylate Surfactants

Dear Barry,

While awaiting your pink sheet, we are investigating surfactants in nonpolar media using ^{1}H and ^{13}C NMR. In an effort to observe the effect of micellization on ^{13}C chemical shifts we have varied the concentration of surfactant from below the critical micelle concentration (CMC) to above it. In general, the observed ^{13}C chemical shifts of hexylammonium propionate (HAP) move upfield with increasing concentration. Plots of observed ^{13}C chemical shifts versus reciprocal surfactant concentration show a break at about 1 M. Similar behavior has been observed for butyl and dodecylammonium propionates in $CDCl_3$.

In addition to chemical shift data we have determined ^{13}C spin lattice relaxation times of surfactants. T_1 data for HAP and DAP are given in the Table. The ^{13}C relaxation times of the alkyl ammonium ions show a general increase in going from the polar ammonium group to the terminal methyl group. The three carbons of the methyl tail have longer relaxation times than the carbons closer to the polar head group of these surfactants. This indicates that these three terminal carbons at the hydrophobic end of the chain have greater mobility than the internal chain carbons which is completely consistant with the formation of reversed micelles in apolar and dipolar aprotic solvents.

Table

^{13}C Chemical Shifts and Spin Lattice Relaxation Times in $CDCl_3$ at 28°

1.189 M DAP		2.0 M HAP	
δ, ppm[a]	T_1, sec	δ, ppm[b]	T_1, sec
181.991	3.924	182.0911	3.704
39.557	0.110	40.6390	0.242
32.048	2.354	32.4108	1.087
31.219	0.764	31.1546	0.799
29.756	0.622	28.9561	0.654
29.610	0.711	27.4487	0.555
29.512	0.763	23.5543	1.566
29.317	0.171	14.9491	2.597
28.293	0.308	11.3061	2.358
26.879	0.214		
22.832	2.025		
14.201	4.695		
10.885	4.114		

[a]Chemical shifts calculated using 1940 Hz (77.494 ppm) for the center plot of $CDCl_3$.

[b]Chemical shifts relative to external TMS contained in Wilmad WGS-10BL coaxial tube.

Sincerely yours,

Steven Rosenthal

S. N. Rosenthal

Ellie Fendler

E. J. Fendler

COLORADO STATE UNIVERSITY
department of chemistry
FORT COLLINS
COLORADO
80521

October 30, 1974

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Title: ^{67}Zn NMR, Postdoctoral Position

Dear Barry,

During the past few months, Larry Simeral, who has been finishing his Ph.D. research in our group, has been carrying out some exploratory ^{67}Zn nmr studies. Aside from a brief report by Epperlein, Kruger, Lutz and Schwenk,[1] there do not seem to be any reported detections of ^{67}Zn nmr signals in liquid samples. A pulse FT approach at 5.63 MHz has been employed for our studies, using a broad-band spectrometer configuration to be described in detail elsewhere.[2] Basically, the spectrometer configuration is based upon using a synthesizer, a broad-band power amplifier and a broad-band preamp, in connection with the i.f. section of the Bruker HFX-90 spectrometer.

Studies carried out on different zinc electrolytes in aqueous solutions over a range of concentrations show clearly the effect of complexation upon both the chemical shift and linewidth of the zinc resonance. Some of these results are shown in the accompanying table (higher value corresponds to lower shielding). From systematic studies of these types of variations, we are exploring the details of the interaction of Zn^{2+} in a variety of situations. Incidentally, we will probably have a postdoctoral position open for this type of work in a few months.

1. B. W. Epperlein, H. Kruger, O. Lutz and A Schwenk, Phys. Lett., 45A, 255 (1973).
2. H.C. Dorn, L. Simeral, J.J. Natterstad and G.E. Maciel, J. Magn. Resonance, in press.

^{67}Zn Data for Some Aqueous Solutions

zinc solution	^{67}Zn chemical shift	^{67}Zn linewidth
1 M $Zn(NO_3)_2$ in 11.2 M aq. NH_3	288.2 ppm	65 Hz
1 M $Zn(CN)_2$ in 3 M NaCN	283.6	40
1 M $ZnCl_2$ in 12 M HCl	256.6	37
1 M $ZnBr_2$ in 12 M HBr	168.9	46
2 M $ZnCl_2$	93	200
1 M $Zn(NO_3)_2$	0.0	47
2 M $Zn(ClO_4)_2$	-1.4	37
2 M $Zn(NO_3)_2$	-1.9	89
1 M ZnI_2 in 12 M HI	-35.5	70

Sincerely,

Gary E. Maciel
Professor

GEM/ng

THE OHIO STATE UNIVERSITY

October 22, 1974

Dr. B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Notice of Position

Dear Barry:

This Department has a position for someone with an M.S. or Ph.D. in the nmr field, experience with high resolution nmr instrumentation and some familiarity with electronics to be Scientific Manager of our Nmr Laboratory.

The principal responsibilities of the Scientific Manager are to operate the nmr spectral service, train operators, keep an eye on the condition of the instruments and to collaborate with faculty on special research problems including instrument development.

The equipment consists of A-60, A-60-A, MH-100, HA-100, HX-90 (seven nuclei, cw and ft) and Brukerian (multinuclear pulse only) nmr spectrometers respectively. Also there is an Electronics Technician who works only on nmr equipment.

Salary will be commensurate with the applicant's experience. Of course Ohio State University is an Equal Opportunity employer.

Interested persons should send me a resumé with names of three references.

Sincerely yours,

Gideon

Gideon Fraenkel
Professor of Chemistry

GF:es

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The two spectra of Δ^9-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 μg of sample in a 1-mm tube) and Spectrum C (20 μg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

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The sample volume in the 1-mm Insert is so much less than the 400 μl required for 5-mm tubes that use of deuterated species becomes more economical.

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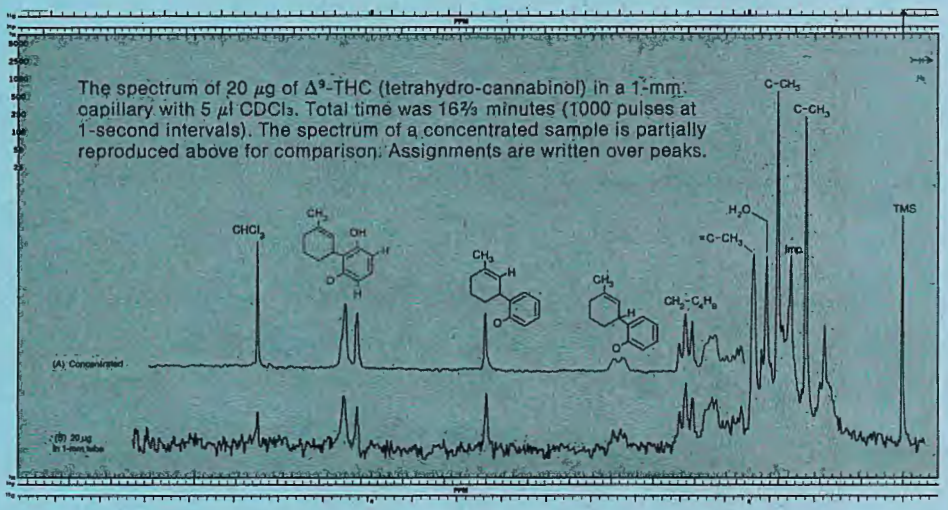

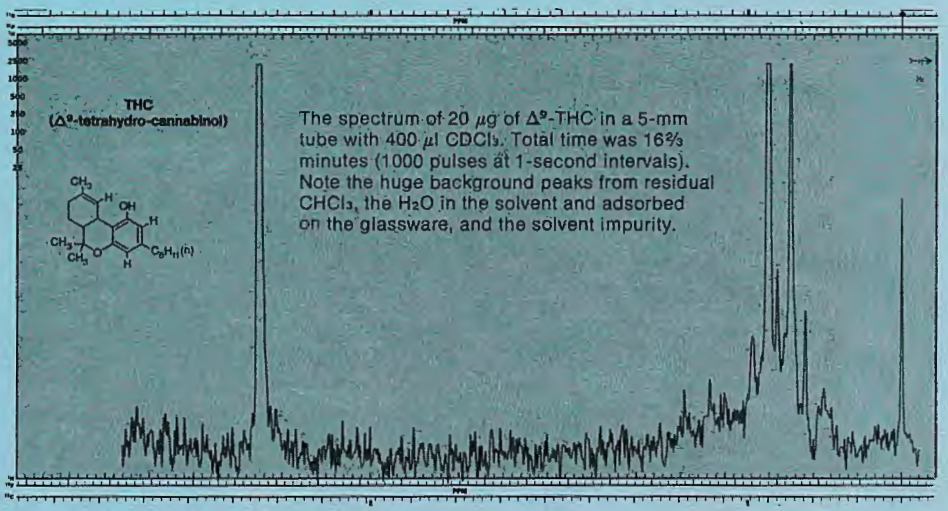

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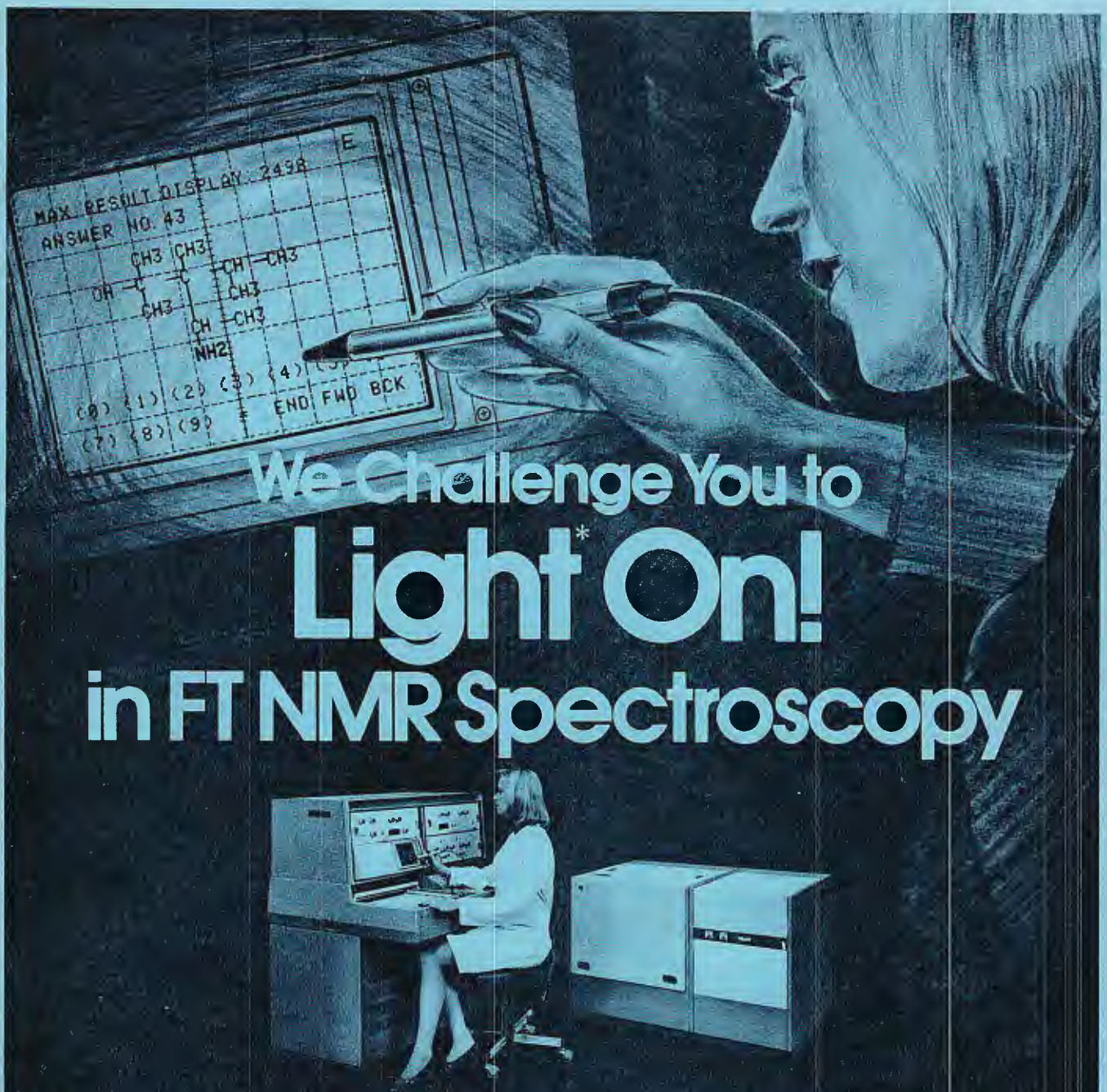

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