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No. 42

DEADLINE FOR NEXT ISSUE

APRIL 25, 1962

AN NMR MICROCELL

J. N. Shoolery, Varian Associates, Palo Alto, California

The problem of sensitivity in NMR spectroscopy has always been a stumbling block to the solutions of problems involving very limited quantities of sample. Various schemes have been proposed for alleviating this difficulty, all of which involve shortening the column of liquid in order to increase the concentration of nuclei in the immediate vicinity of the receiver coil where they will induce the largest signal voltage. These schemes are all limited by the loss in resolution which results from allowing the nuclei near the ends of the column to contribute to the observed signal, since these nuclei are in a less homogeneous field due to the distortion arising from the discontinuity of the magnetic susceptibility. The cylindrical nylon plugs described in Vol. 2, No. 3 of the Varian Technical Information Bulletin tend to minimize this difficulty but the sensitivity enhancement of approximately a factor of two has been largely offset by the difficulty of use.

The need to spin the sample and the consequent tendency to form a flux-distorting vortex dictate the employment of some means of confining, or trapping, the sample within the receiver coil. It can be shown that the field within an ellipsoidal cavity of revolution is uniform if the field in the surrounding medium is initially uniform before introduction of the cavity. The simplest such cavity is a sphere, which can be formed by juxtaposition of two plugs with hemspherical cavities. We have pursued this approach in our laboratories to the point that it now appears practical to obtain quite usable spectra of sub-milligram quantities of samples in the 300-400 molecular weight range. A single proton, unsplit by spin-spin coupling, should be observed readily with one micromole of sample. The microcell is assembled by inserting two plugs with hemspherical cavities facing one another into one end of an A-60 precision pyrex cell, open at both ends and ground slightly to remove sharp edges from the inside and outside of the openings. The upper plug differs from the lower one in having a #80 drill hole along the longitudinal axis. It is most convenient to place the sample directly into the cavity of the lower plug before assembling, but it can be dissolved in the solvent first if necessary.

The volume of the cavity and axial filling hole is almost exactly 25 microliters. This amount of $CDCl_3$ is pipetted onto the top of the upper plug. A tool with a small hook is inserted into the recess in the bottom of the lower plug, and by engaging the .040 drill hole one can move this plug downward to draw the solvent through the axial filling hole in the upper plug (See Figure 1). Pushing the lower plug upward into contact with the upper plug forces the air out of the cavity and traps the sample in the spherical cavity. The entire assembly can be pushed up or down to position the cavity about 15 mm. from the lower end of the cell.

It has been found that the volume susceptibility of $CDCl_3$ is almost exactly equal to that of nylon. Furthermore, although $CDCl_3$ causes slight swelling of nylon, it does not seem to attack it, at least over periods of a few days. Since most NMR spectral data are catalogued as solutions in either CCl_4 or $CDCl_3$, these solvents are particularly recommended for use with these plugs.

We have found that the cavity can be positioned within the receiver coil by parking the spectrometer on a strong peak in the spectrum and adjusting the A-60 tube in the spinner for maximum signal. The spinner can be taped to the tube to assure proper positioning if the cell is removed and replaced.

If solutions of equal concentration are placed in the microcell and in an ordinary cylindrical A-60 cell, the signal from the microcell is found to be about

1/3 as strong as the conventional cell. This is due to the fact that not all of the volume seen by the receiver coil is occupied by sample when the length of the column is restricted by plugs. For a fixed quantity of sample, however, the concentration is increased by approximately 15-fold, resulting in a net gain of sensitivity of approximately 5.
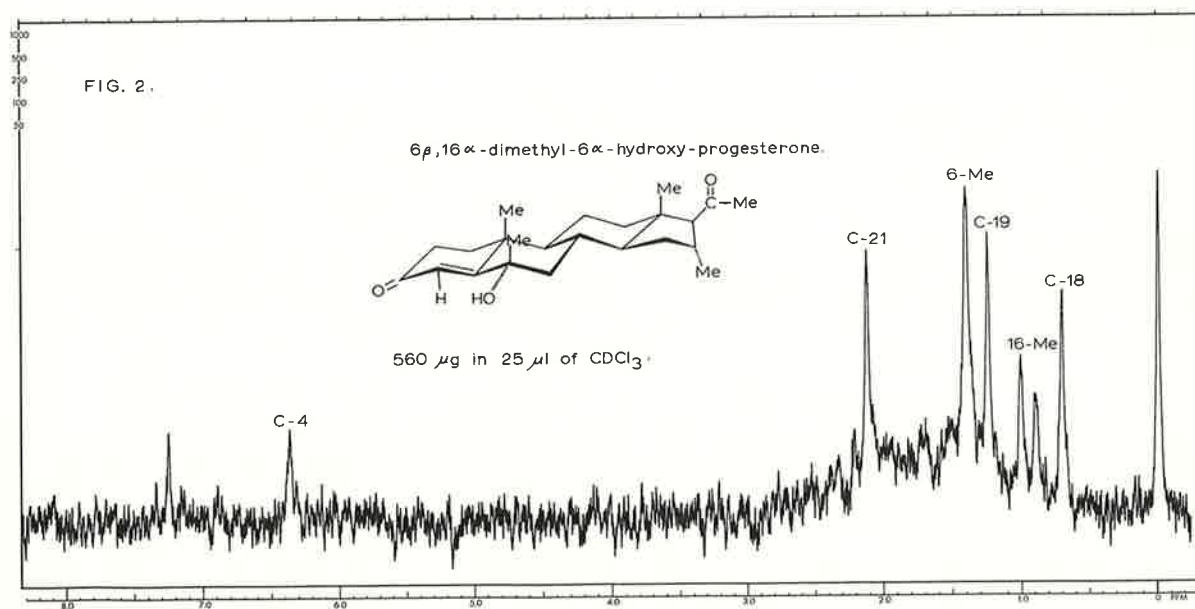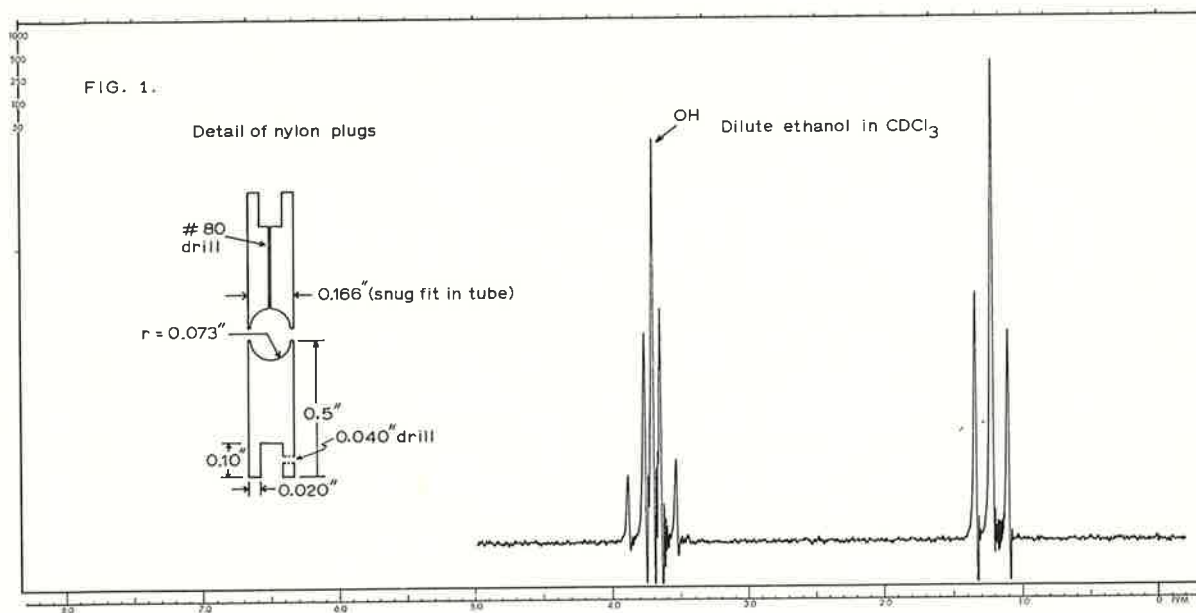
Due to the rather considerable increase in concentration, it is important not to use more than 2-3 milligrams of sample in most cases, since excessive concentration will lead to high viscosity and detrimental line broadening. Not all samples will be soluble enough to permit this degree of concentration (about 10 per cent). However, we have found that excellent results can be obtained by spacing the plugs 8 mm. apart. This permits essentially the entire active volume of the coil to be filled with sample and increases the concentration and consequently the signal strength by 3-fold over the conventional manner of filling. The solubility requirements are thus seen to go up much faster than the gain in signal strength after a 3-fold enhancement is reached. We are planning to plot the signal intensity against the distance of separation of the plugs for both constant concentration and constant quantity of sample in order to determine more readily for each sample the optimum mode of operation.

The resolution which can be obtained with the spherical sample appears to be very nearly as good as with the conventional cylindrical sample if the cell is carefully positioned. Slight adjustment of the fine Y-axis shim current may be required. Some change in the curvature control setting is sometimes desirable and varies from one set of plugs to the next. We believe that if the plugs are made sufficiently accurately that adjustment of the curvature control will be minimized or may even be unnecessary. Figure 1 shows the spectrum of a dilute solution of ethanol in $CDCl_3$ with the plugs in contact with one another. With 8 mm. separation of the plugs, still better resolution is obtained, essentially equivalent to that obtained with the conventional cell.

Figure 2 shows the spectrum obtained with 560 micrograms of 6β, 16α-dimethyl-6α-hydroxy-progesterone. This spectrum was obtained with an A-60 spectrometer using a scan time of 500 sec. Several practical problems have recently been solved in our laboratory with total samples of about one milligram. Sample handling operations now appear to represent the greater part of the effort expended in getting the NMR data on a limited sample.

Nearly quantitative sample recovery can be accomplished by simply pushing the entire assembly out of the tube into a small vial and rinsing the cell and plugs into the same vial. The plugs can be reused a number of times after rinsing and drying.

Materials other than nylon can doubtless be used. We have found that Delrin works well initially but is swelled by the solvent to the point of bursting the glass tube. We plan to try a variety of plastics in the near future. Our experience has led us to believe that the homogeneity of the field in the cavity and the ease of manipulating the assembled cell are both proportional to the degree of machining accuracy achieved in the manufacture of the plugs. It is not recommended that the job be attempted by other than an expert machinist.

FIG. 1.

Detail of nylon plugs

80 drill

0.166" (snug fit in tube)

r = 0.073"

0.5"

0.040" drill

0.10"

0.020"

OH

Dilute ethanol in CDCl$_3$

FIG. 2.

6β,16α-dimethyl-6α-hydroxy-progesterone.

Me

Me

Me

C—Me

O

O=

H   HO

Me

560 μg in 25 μl of CDCl$_3$

C-4

C-21

6-Me

C-19

C-18

16-Me

BOX 731 DURHAM, NORTH CAROLINA
March 20, 1962

Dr. A. A. Bothner-By
Director of Research
Mellon Institute
44 W. Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Bothner-By;

I would like to describe a modification of the Varian Variable
Temperature Accessory which we feel extends its usefulness.
Two objections to Varian's unit which our modification overcomes
are: (1) the need for auxiliary ventilation (i.e.) the fan, and
(2) the involved exit route of exhaust gases.

Our modification (see figures) consists of: (1) a doughnut
shaped teflon cap which fits over the insert and beneath the
spinner and permits the exhaust gases to be drawn directly out
the rear of the probe - a slight vacuum on the exhaust line
facilitates the gas removal, and (2) channels drilled in the
body of the variable temperature block through which a liquid
is pumped to either heat or cool the entire probe, depending
upon the temperature region under investigation.

Tests indicate that for high temperature experiments this
modification significantly reduces the temperature rise in the
probe, as measured at the male insert coaxial connector in the
probe.

VARIABLE TEMPERATURE UNIT

Modified		Unmodified	
Probe Temp.	Sample Temp.	Probe Temp.	Sample Temp.
28°C	210°C	41°C	204°C

Enclosed are 60 M.C. spectra obtained using our modified
variable temperature accessory. Temperature is 220°C,
material is a 10% solution of stereoregular polystyrene
in CCl4.

I apologize for the extreme tardiness of our contribution
but hope to have other contributions in the near future.

Yours sincerely,

Wallace C. Lawrence

W. C. Lawrence
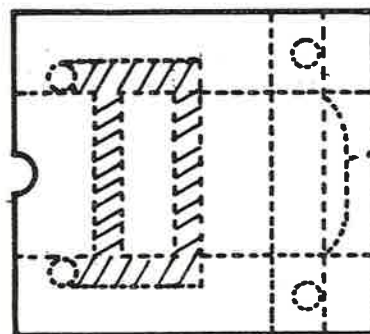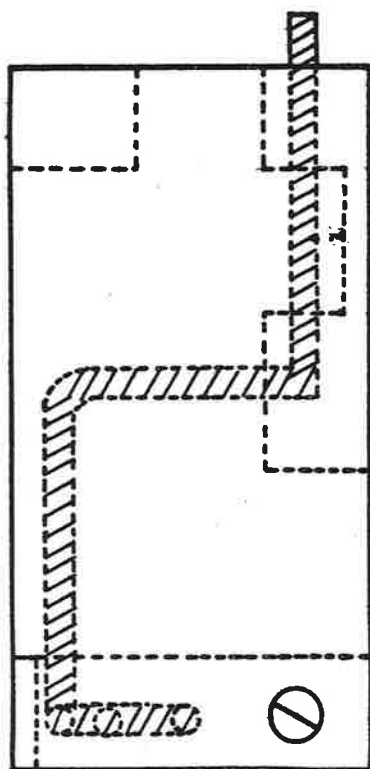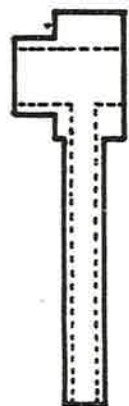Basic Research Dept.
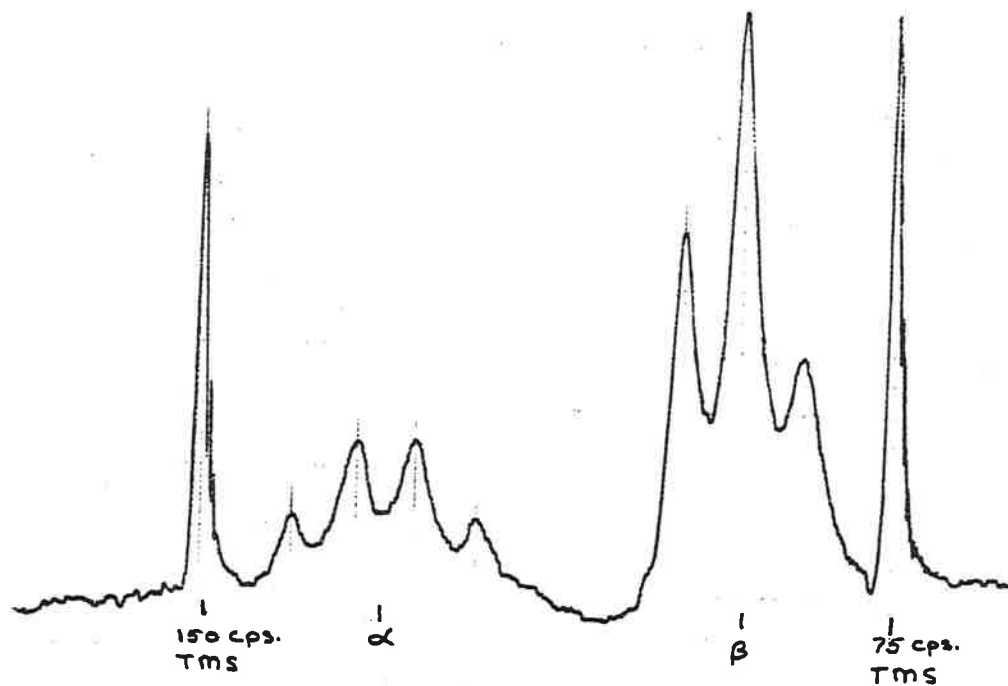
Enclosures

BR/62-121/tc

DUKE
DURHAM

RESEARCH

N. C.
CHAPEL
HILL

TRIANGLE
PARK

N. C. STATE
RALEIGH

STEREOREGULAR POLYSTYRENE @ 220°C. in CCl₄

450 cps. TMS

m-, p-

o-

375 cps. TMS

150 cps. TMS

α

β

75 cps. TMS

VARIAN
associates
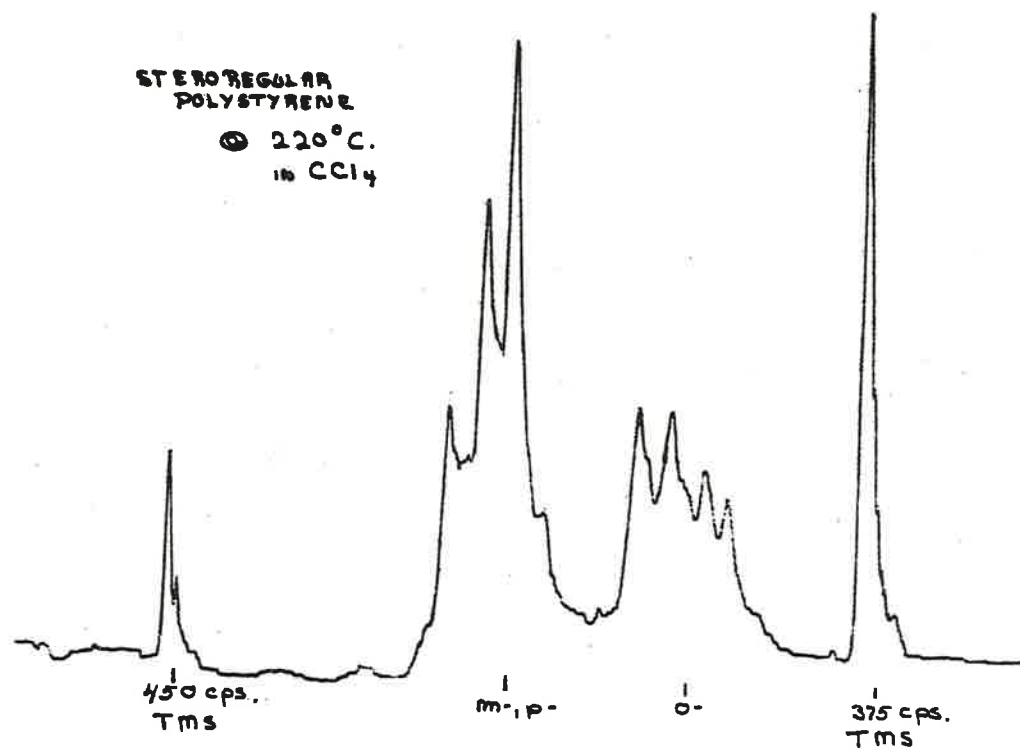
Professor A. A. Bothner-by
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Professor Bothner-by:

A LONG-RANGE COUPLING

Often it is the simplest of molecules that provides the most in-
teresting NMR spectrum; we found recently that even long-suffering acet-
aldehyde can be made to yield some interesting new data in the form of
nuclear Overhauser effects. But that is another story....We would like
to mention here one feature of the spectrum of methyl salicylate (degassed
1:1 solution in carbon tetrachloride) and confess our surprise on finding
that the phenolic proton couples to the proton (R) in the meta position
across the ring. J = 0.4 cps. We are unaware of any reported examples
of other phenolic protons coupling in this way, but perhaps your readers
will correct us on this point if we have overlooked something.

To avoid any possible confusion with the small para coupling in
the ring, we removed the splitting in the R part of the spectrum first by
strong irradiation of the hydroxyl proton and then by adding a few drops
of acid to accelerate the hydroxyl exchange. The figure shows the normal
spectrum of OH (a) and the ring proton R (b) together with the R spectrum
under double irradiation conditions (c) and in the acidified sample (d).
Feeling more ambitious, we decided to try a temperature study to see if the
OH line decouples or shifts or both as the temperature is raised. Although
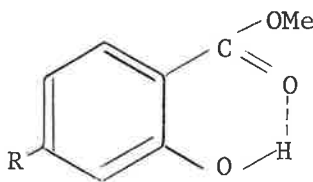it is clear that more work is necessary on this aspect, we feel we can say
with a fair amount of confidence that above 145°C the sample explodes (but
appears to retain the coupling).

There seem to be a few examples of aldehyde protons that couple into
aromatic rings, and in certain cases this is not to the ortho proton. One
example is fural (Leane and Richards, Trans.Faraday Soc., 55, 518, (1959));
another is pyridine 3-carboxaldehyde (Kowalewski and Kowalewski, J.Chem.Phys.,
36, 266, (1962). For methyl salicylate, it is interesting to speculate on
(a) why the phenolic proton couples at all, (b) why it should be the meta
proton that is chosen. One cannot help feeling that the constraint imposed
by the intramolecular hydrogen bond has some influence on question (a). We
would welcome any comments from readers. We are writing this up as part of an
analysis paper in which we have justified our assignment of proton R.

Yours sincerely,

N.S. Bhacca, R. Freeman
Varian Associates
Instrument Division

NSB/RF:jl
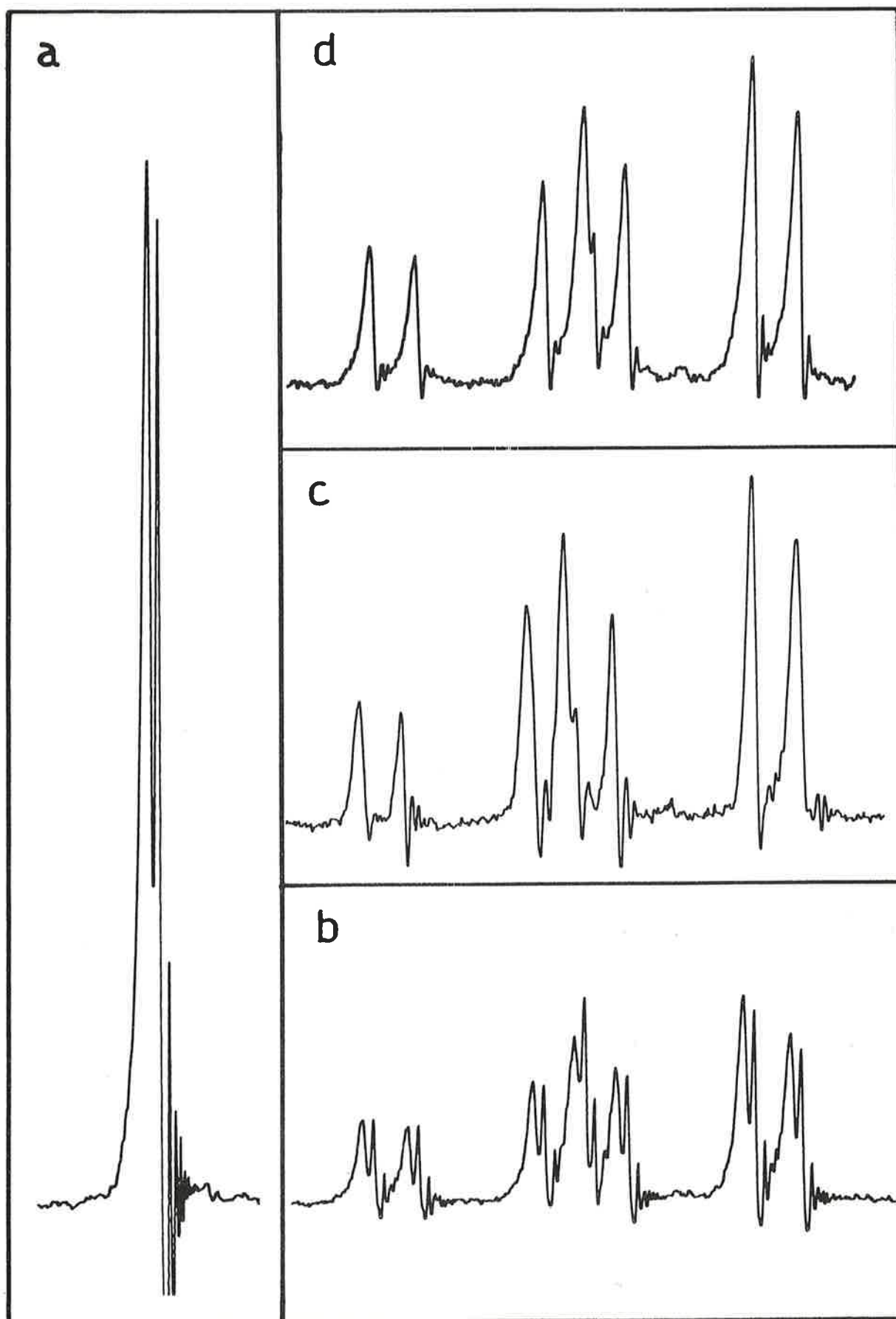
C^{13} NMR Studies Using

the Absorption Mode

J. N. Shoolery, Varian Associates, Palo Alto, California

Due to the long thermal relaxation times associated with C^{13} nuclei, it has been customary to study natural abundance samples with the adiabatic rapid passage method. This gives a signal proportional to Mo, the static moment/unit volume, while the absorption mode gives a signal proportional to $\frac{Mo}{2}\sqrt{T_2/T_1}$ for slow passage conditions. Rather considerable line broadening occurs as a result of the high r.f. power required for adiabatic conditions and this not only obscures the smaller splittings due to spin-spin coupling but makes it difficult to interpret overlapping multiplets.

The need for a large sample is a result of the 1.1% natural abundance of C^{13}. Until recently it has not been practical to spin a large sample under conditions of very high r.f. amplification because the rotation of the sample introduces a varying coupling between the transmitter and receiver of sufficient magnitude to overload the detector. A static sample results in T_2 being about two orders of magnitude shorter than T_1. With modulation techniques which have been developed for stabilizing the baseline to permit integration of spectra, spinning a large sample is now practical, since the NMR signal is now observed as a modulation on the r.f. output of the receiver coil. Less r.f. gain is required because the signal can be amplified in a subsequent audio amplifier, and r.f. fluctuations at the spinning frequency can be distinguished from the modulation frequency through use of a phase sensitive detector.

An instrument operating at 15.085 mc/sec in a magnetic field of 14,092 oersteds was employed in this work. A special receiver coil was constructed by winding a coil on the inside of a cylindrical glass support with i.d. of 14 mm. Thin-walled cells were obtained from the Wilmad Glass Company, Buena, New Jersey, with i.d. of 11 mm and o.d. of 12 mm. A plastic spinner obtained from the same source provided a satisfactory means of rotating the cells at about 30 r.p.s. A cylindrical teflon plug was made which could be fitted into the cell at the liquid interface to prevent formation of a vortex. With this arrangement it was possible, by careful adjustment of the Homogeneity Control Unit, to achieve an effective T_2 of 2-3 sec., observed by the exponential oscillatory decay following the signal from a strong, single C^{13} resonance line.

The signal-to-noise situation is made still more tolerable by the fact that more than adequate resolution is achieved without the necessity of meeting the slow passage conditions. Under the non-adiabatic rapid passage conditions actually used, the role of T_1 in repopulating the lower energy levels is not as important; i.e., we can use more r.f. power and leave the nuclei in a partially saturated condition, at the expense of some line broadening but with a gain of signal strength. Sweep rates of about 1 cps were used for most of

this work which resulted in spending a small fraction of T_1 in observing
each C^{13} resonance line.

A standard integrator accessory was used which employs 2000 cps field
modulation. Instead of observing the center-band signal as with protons,
the side-band signals were recorded. This made possible a much lower index
of modulation. Center-band signals can be suppressed by adjustment of phase,
while second side-band signals are lost in the noise, due to the low modula-
tion index. Thus, no interference is caused by the modulation unless the
interfering signals are 4000 cps (400 ppm) apart.

With this apparatus, previously unresolved spin-spin splittings were
readily observable. Fig. 1 shows the spectrum of acetic acid. The C^{13} in
the carboxyl group is found to be a quartet with spacing corresponding to
J = 7.5 $\pm$ 0.5 cps, due to the protons on the adjacent carbon atom. The di-
rect J_{CH} coupling is 132 cps.

Fig. 2 shows the spectrum of ethanol. The methyl carbon is split into
a quartet with a 125 cps coupling to the attached protons, and less than 2 cps
coupling to the methylene protons. On the other hand, the methylene carbon
shows a 140 cps coupling to its own protons (enhanced by the attachment to oxy-
gen) and a 4.5 $\pm$ 0.5 cps coupling to the methyl protons. The chemical shift
between the two carbons is 38.5 ppm.

An excellent example of the data obtainable in this way is found in pyri-
dine. Fig. 3 shows the spectrum with the β carbons falling at the highest field
value, the γ carbon 11.8 ppm to lower field, and the α carbons 26.0 ppm to lower
fields. The direct C^{13}-H couplings are 180, 157, and 160 cps for the α, β, and
γ carbons respectively. The α carbons are coupled to two other protons, prob-
ably the β proton and either the γ or the other α proton, with coupling constants
of 11.0 and 6.2 cps. The β carbon is coupled about equally to the α and γ pro-
tons with J = 8.0 cps. Finally, the γ carbon is coupled to the β protons with
a 5.8 cps coupling constant, and is apparently not coupled to the α protons.

Chemical shift measurements and initial location of the peaks would be
improved by collapse of the spin-spin multiplets to a single line by double ir-
radiation techniques. Since apparatus for this purpose was available, the exper-
iment was tried with a 4 mm sample of methyl acetylene enriched to 50% C^{13} in the
methyl position. The spectrum with and without 60 mc irradiation is shown in
Figure 4. In addition to the signal-to-noise enhancement of 16/3 due to the col-
lapse of the 8-line multiplet, there is an additional Overhauser amplitude enhance-
ment of 1.5 due to relaxation of the C^{13} nuclei through the proton magnetic mo-
ments. The effect may be greater than 1.5 and could best be measured from the
integral, since the collapse of the multiplet does not appear to be complete at
the power level used.

FIG. 1

C^{13} NMR SPECTRUM OF ACETIC ACID (15.085 mc/sec)
(Natural abundance)

CH$_3$–C^{13}OOH

J$_{C-C-H}$ = 7.5 ±0.5 cps

C^{13}H$_3$–COOH

J$_{C-H}$ = 132 cps

——— 158 ppm ———

—H→

FIG. 2

C^{13} NMR SPECTRUM OF ETHANOL (15.085 mc/sec)
(Natural abundance)

C^{13}H$_3$ C^{12}H$_2$ OH

J$_{C-H}$ = 125 c/s

J$_{C-C-H}$ < 2 cps

C^{12}H$_3$ C^{13}H$_2$ OH

J$_{C-C-H}$ = 4.5 ±0.5 cps

J$_{C-H}$ = 140 c/s

——— 38.5 ppm ———

←H—

FIG. 3

C^{13} NMR SPECTRUM OF PYRIDINE (15.085 mc/sec.)
(Natural abundance)

|←——— 180 ———→| |←——— 160 ———→| |←——— 157 ———→| J_{C-H} (cps)

J_{C-GH} = 11.0 cps
$J_{C-?-C-H}$ = 6.2 cps

J_{C-C-H} = 5.8 cps
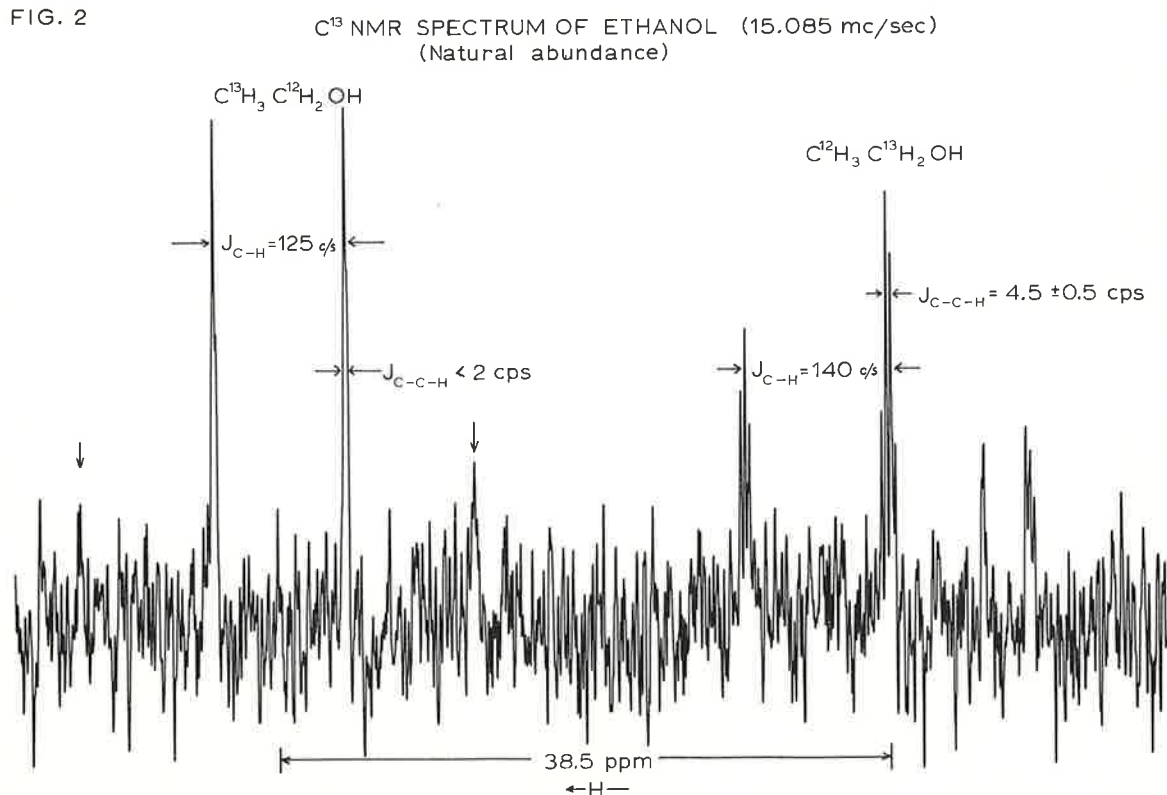
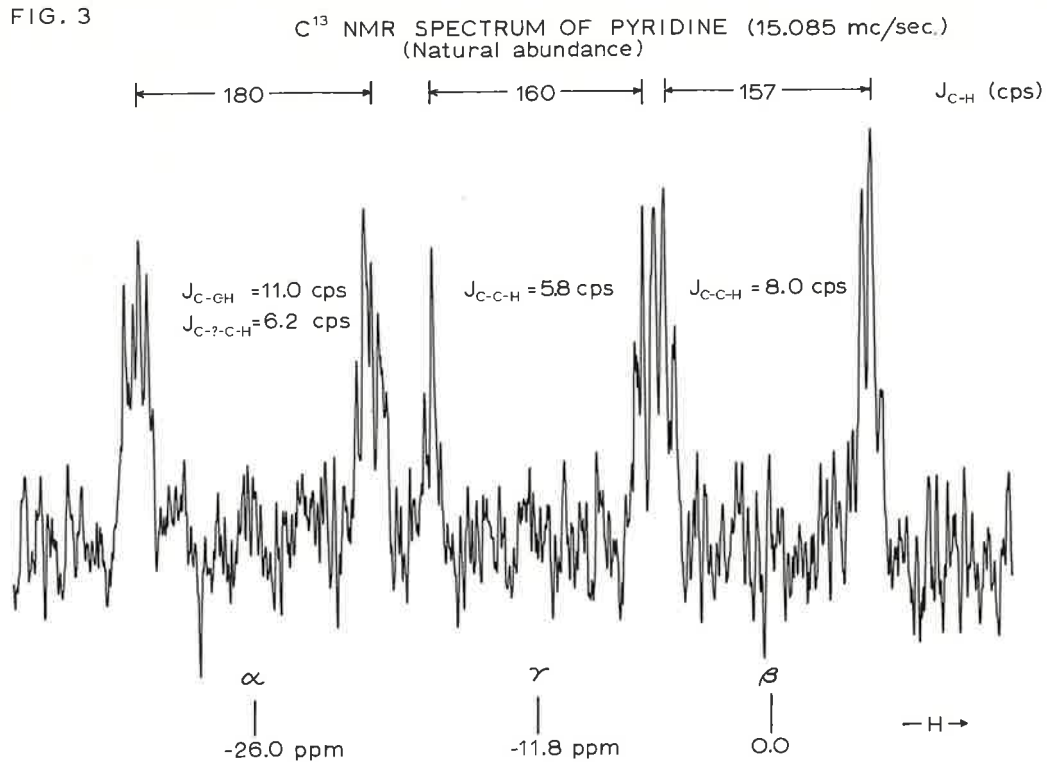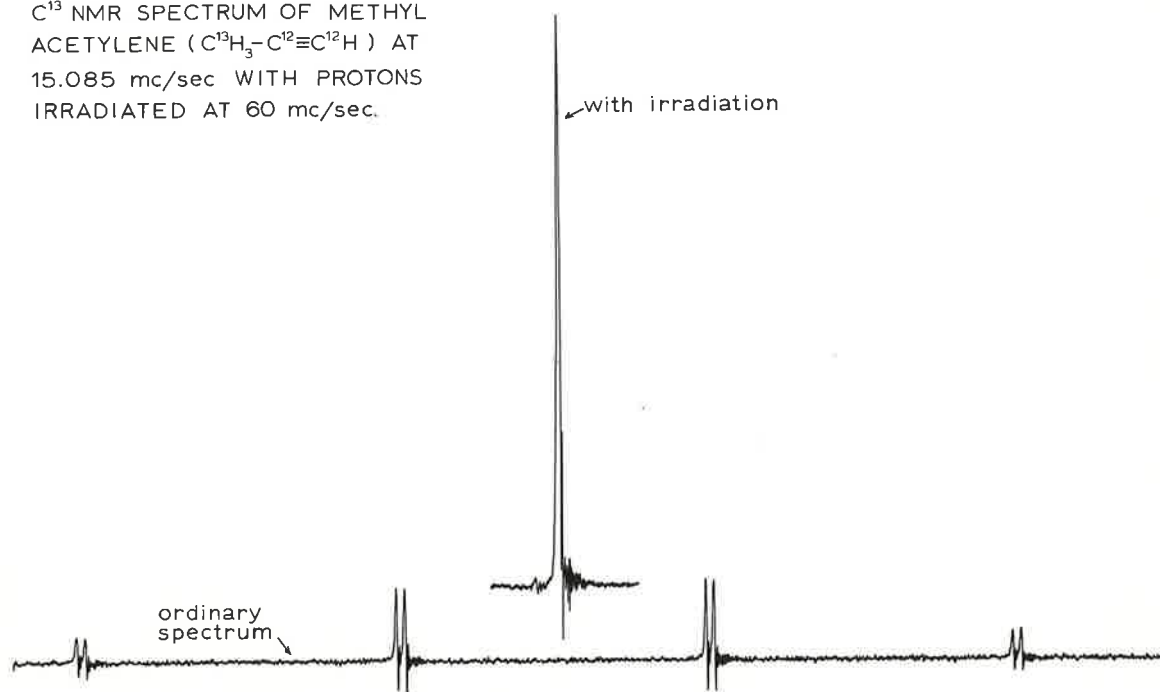J_{C-C-H} = 8.0 cps

α

γ

β

—H→

-26.0 ppm

-11.8 ppm

0.0

FIG. 4

C^{13} NMR SPECTRUM OF METHYL
ACETYLENE (C^{13}H$_3$–C^{12}≡C^{12}H) AT
15.085 mc/sec WITH PROTONS
IRRADIATED AT 60 mc/sec.

with irradiation

ordinary
spectrum

UNIVERSITE DE MONTPELLIER

ÉCOLE NATIONALE SUPÉRIEURE
DE CHIMIE
———
8, RUE DE L'ÉCOLE-NORMALE
TÉLÉPHONE 72.49.19

Montpellier, le 9th March 1962

Dr. A.A. Bothner-By,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, 13.
Penn.

Dear Dr. Bothner-By,

We have been working recently on a certain number of diazole derivatives and would like to observe the spectra at low temperatures.

The problem is this. Pyrazole and imidazole show no long range coupling with the nitrogen proton, whereas it has been shown that pyrole gives coupling of the N proton both with α and β protons. We want to know if the non observance of the N proton coupling is due to rapid exchange of this proton with other molecules or whether it comes from the absence per se of a coupling constant. We thought the best way to see this would be to examine the spectra in very anhydrous conditions and at low temperatures.

As we are not equipped for the moment with a low temperature probe we are wondering if you could see your way to examining this for us. We should be extremely grateful if this were possible. However, if you cannot find time yourself to help us out of on this perhaps you could put this letter in MELLON-M-R.

Yours sincerely,

Robert Jacquier
Professeur à la Faculté des
Sciences

James Wylde
Chargé de Recherches, C.N.R.S.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

March 21, 1962

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Aksel:

We have recently examined the H^1 and F^{19} spectra of a variety of simple fluorinated hydrocarbons in the gas phase. We feel that the spectra of molecules containing groups of equivalent F^{19} nuclei may be of particular interest to MelloNMR readers.

The proton spectrum of difluoromethane at about 3 atm. is shown in Figure 1. Instead of a simple 1:2:1 triplet that one might expect to find, the spectrum consists of three broad lines of equal intensity, with a sharp peak superimposed on the central broad line. The methyl group resonance of 1,1 difluoroethane at about 3 atm. is shown in Figure 2. For this example, the spectrum includes three broad peaks, with a sharp doublet superimposed on the central broad line. The resonance of the 1-proton also consists of three broad lines, with a sharp quartet superimposed on the central broad line.

We suggest that the line width of the multiplets in the proton spectra of these molecules is determined primarily by the F^{19} relaxation time. Furthermore, the F^{19} relaxation times must be considerably different for the singlet and triplet arrangements of the F^{19} spins. Thus, in the triplet spin state, the F^{19} relaxation times are short, giving rise to the three broad multiplets in the proton spectra. In the singlet state, the F^{19} relaxation times are long, giving the narrow line for CH_2F_2, and allowing resolution of the splitting of the $-CH_3$ resonance by the 1-proton in CH_3CHF_2.

The above interpretation of Figures 1 and 2 requires that the F^{19} relaxation times be considerably less than the H^1 relaxation times, at least for the triplet F^{19} spin states. Johnson, Waugh, and Pinkerton (J.C.P., 35, 1128 (1961)) have noted that the dominant F^{19} relaxation mechanism in CHF_3 arises from the large F^{19} spin-rotation interaction. However, the proton spin-rotation interaction in CHF_3 is apparently small, and the proton relaxation time is determined by the usual dipole-dipole mechanisms. A large F^{19} spin-rotation interaction could easily account for the short F^{19} relaxation times (for the triplet states) in CH_2F_2 and CH_3CHF_2.

We are currently calculating in detail the contributions of the various relaxation mechanisms for the simpler molecules. We also have additional experimental work in progress to confirm the origin of these effects.

Yours very truly,

George W. Flynn
George W. Flynn

John D. Baldeschwieler

GWF/JDB:br
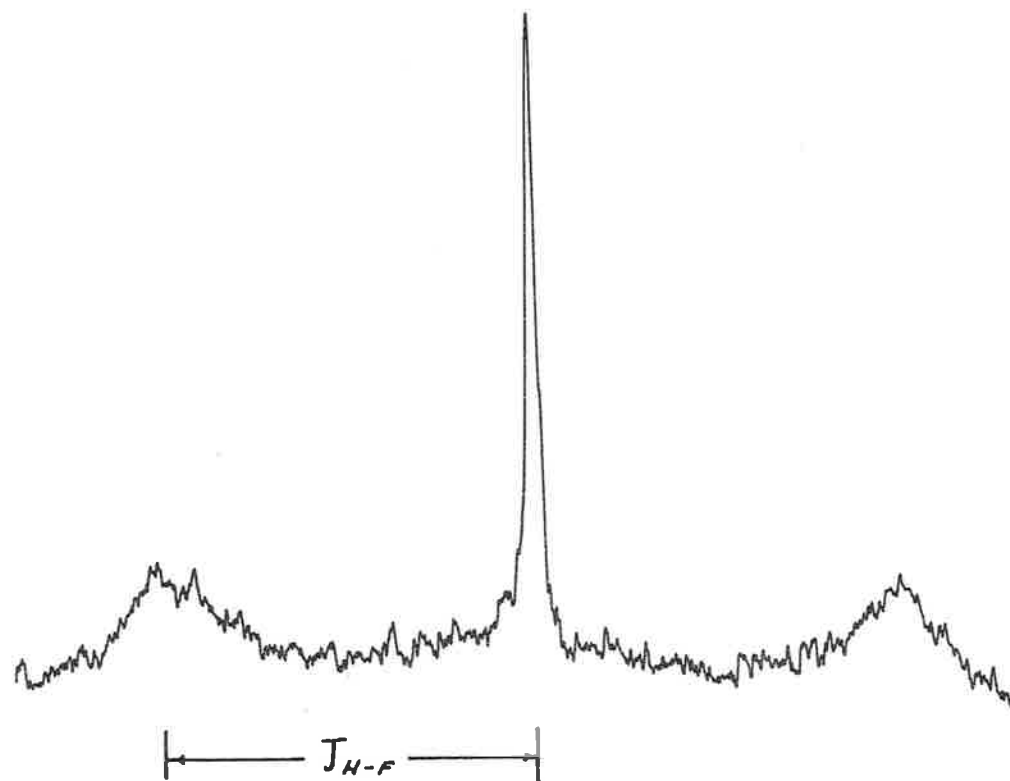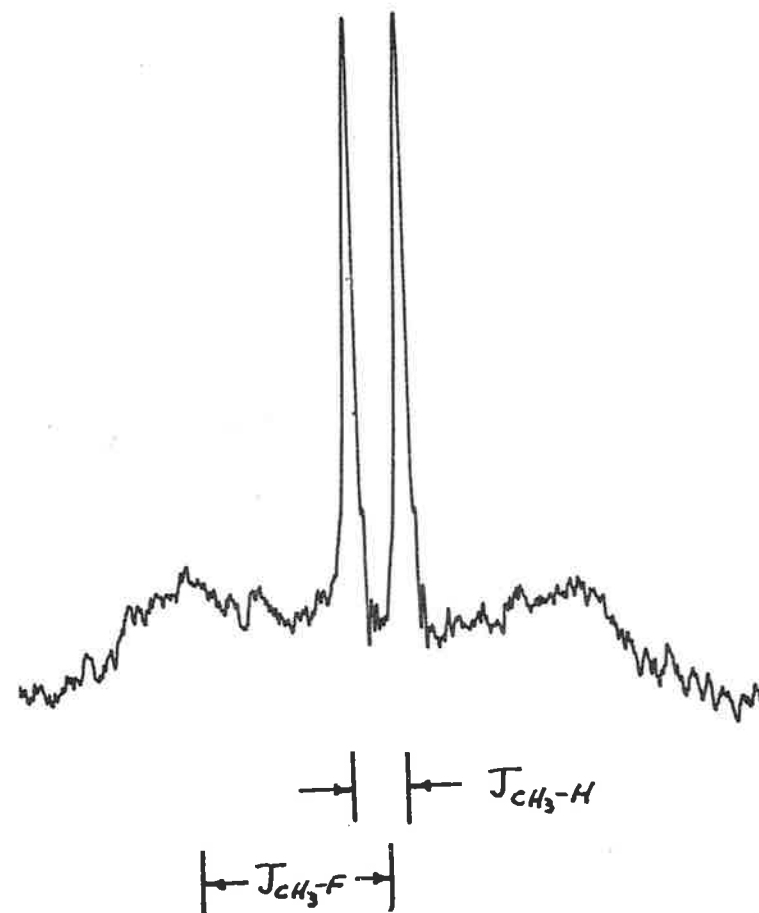
Fig. 1

Fig 2

J_{H-F}

J_{CH_3-H}

J_{CH_3-F}

4-13

DARTMOUTH COLLEGE
DEPARTMENT OF CHEMISTRY
HANOVER · NEW HAMPSHIRE

20 March 1961

Dr. Aksel A Bothner-By
Mellon Institute
Pittsburgh 13, Pennsylvania
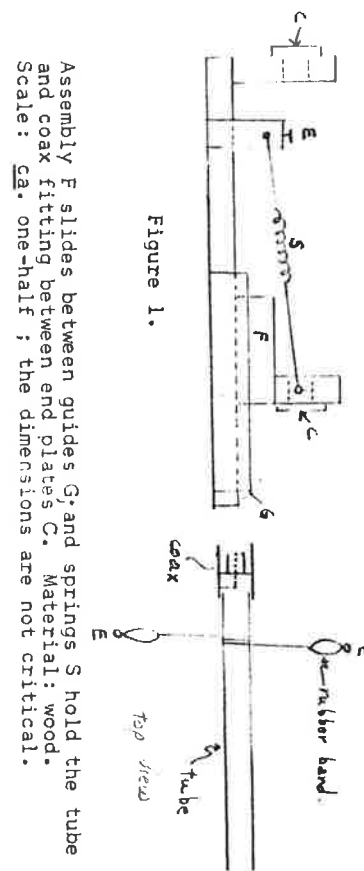
Dear Dr. Bothner-By:

From time to time it is nice to be able to make a high
resolution insert on short notice. My first dozen tries were
failures. Some were esthetically pleasing to the eye, most
balanced sharply and had good sensitivity, but unhappily they
also split all lines into doublets (J about 2 cps). The effect
of this on an ABC_3 system must be seen to be appreciated. The
following procedure, however, has worked (two in succession),
the resolution and sensitivity are essentially the same as
obtained with the commercial insert, and it is simple enough
not to require a large investment of time.

Wind uninsulated, oxygen free, high conductivity copper
wire (OFHC, 30 gauge) around the tube (1), spacing the turns with
fine thread, and secure the ends to the side posts of the jig
(fig 1) under tension from small rubber bands. Warm to about
60°, coat very lightly with resin (2) and heat about two minutes
at 100° until resin in tacky. Remove the thread, give a second,
light, coat of resin and bake at 100° for thirty minutes. Bend
the leads down the tube, secure the ends with tape, coat with
resin and bake. Trim the leads, solder one to the outside of
the coax fitting (3) with minimum heat and solder, bend the other
to reach the center pin and solder. Put the pin in place,
coat the bottom of the tube with resin (4), assemble in the jig
and bake.

1. Select standard wall pyrex tubing with an ID to give a slip
    fit with the spinner bearing. For variable temperature work, close
one end flat, and pick or drill three 2 mm holes around the tube
as close to the end as permitted by the sides of the spinner
bearing. Clean successively with trisodium phosphate, water,
aqua regia, water and dilute ammonia and bake to dry.
2. Ciba Araldite Resin 6010 cured with hardner Araldite HN 951
    (100/12 pbw).
3. Cut from a UG-262/U plug. Face off the lugs and cut out the
    end to a depth of about 1 mm so the plug fits loosely over
the end of the insert tube. Notch the rim and from this point
cut a channel into the center pin and down to one of the solder
"dimples" on the side of the plug. The depth of the channel is
that of 30 gauge wire to lie flush.
4. A commercial filled resin such as Hysol etc. is preferable.
    The inert (non-metallic) filler gives added dimensional
stability over a wide range of temperature.

Sincerely yours,

Paul R. Shafer

Figure 1.

Assembly F slides between guides G, and springs S hold the tube
and coax fitting between end plates C. Material: wood.
Scale: ca. one-half ; the dimensions are not critical.

NMR PARAMETERS IN CIS AND TRANS 2-FLUORO-3-CHLOROPROPENE-2

C. A. REILLY

A table of some F to F and F to H nuclear spin-spin coupling constants was published in 1956.[1] The assignments were based on the internal consistency of the data together with some theoretical arguments regarding the origin of the interactions.[2] It has been brought to my attention through a recent note by Tiers[3] that confirmatory data for these assignments have never been published. Such data are presented in this note.

The cis and trans isomers of 2-fluoro-3-chloropropene-2 boiling at 30°C and 60°C were obtained commercially.* The higher dipole moment of the isomer with the F and Cl atoms cis to one another should cause this compound to have the higher boiling point. An examination of the infrared spectrum [4] confirms this conclusion because bands nominally assigned to C-F and C-Cl stretching are relatively weak in the lower boiling isomer and strong in the other one. Hence, the structures have been assigned to the isomers as in the Table below.

Proton and fluorine NMR spectra of the neat liquids containing a little tetramethylsilane (TMS) were obtained at 40 Mc/sec in the usual way with a modified Varian V-4310 spectrometer. The spectra had the expected multiplet structure and were analyzed by a simple first order procedure to yield the parameters given in the Table. There was insufficient perturbation in the spectra to allow the relative signs of the J's to be determined.

NMR Parameters for 2-Fluoro-3-Chloropropene-2

	H_3C $\diagdown$ $\diagup$ Cl $C=C$ F $\diagup$ $\diagdown$ H	H_3C $\diagdown$ $\diagup$ H $C=C$ F $\diagup$ $\diagdown$ Cl	
	B.P. 30°C	B.P. 60°C	
$\delta(=CH)$	1.99 ppm	1.92 ppm	Ref. Internal
$\delta(-CH_3)$	5.86 "	5.31 "	TMS
$\delta(-F)$	12.66 "	10.18 "	Ref. External CF_3COOH
J_{FH}	10.8 cps	24.2 cps	
J_{FCH_3}	16.85 "	16.3 "	
J_{HCH_3}	1.14 "	1.26 "	

It is seen that the resonances of both $-CH_3$ and $=CH$ occur at lower applied field when these groups are cis to electronegative groups (Cl and F respectively) than when they are trans. This is in agreement with the findings for other olefins.[5,6] It is also evident that the magnitude of the trans coupling between F and H is more than double that of the cis coupling. The consistency of this result with those reported previously[1] serves as a confirmation of the assignments made in the early work.

It is also noted that the magnitude of the trans coupling between H and CH_3 is slightly smaller than that of the cis coupling. This in in agreement with that found for propylene.[7] Similarly, it has been found that the cis F to CF_3 coupling[8] as well as the cis CF_3 to CF_3 coupling[3] is larger than the trans. It appears that when the coupled nuclei (F or H) are both attached to an unsaturated C atom the trans coupling is larger than the cis. On the other hand, if one or more of the coupled nuclei are attached to a saturated C atom, the situation is reversed and the cis coupling becomes the larger.

---

* Halogen Chemicals, Inc., Columbia, S. C.

DEFENSE PRODUCTS DIVISION FAIRCHILD CAMERA AND INSTRUMENT CORPORATION
300 ROBBINS LANE, SYOSSET, LONG ISLAND, NEW YORK
WELL 1 4400 • TWX OY UY 676 • Cable FAIRCAM SYOSSET NEW YORK

March 20, 1962

Dr. Barry Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Barry:

Here is my long-overdue contribution to MELLONMR.

It may be of interest to HR-60 users to know about the availability of some items for the alteration of their field homogeniety controls. As we wanted to leave our FHC on at all times, it was necessary to replace the batteries. We have replaced the batteries with a transistorized D.C. power supply manufactured by Technipower, Inc. So. Norwalk, Conn. It is their Model M1.5-0.375 transistor D.C. power supply, priced at $75.00. This is the unit now installed in the current FHC unit sold by Varian. We also found it desirable to replace their Y control with a 10-turn helipot and our curvature control with a dual 10-turn potentiometer. The latter unit is manufactured by Spectrol Electronics Corp., Plainview, L. I., New York. Any correspondence regarding this unit should be addressed, "Attention: Mr. Swinarski". The order should read, "one (1) Model 500, Dual (10-turn) Potentiometer, 500 ohms/potentiometer". This unit costs $35.00. We have also used one of their Model 30 Dial, which costs $5.75. The dual potentiometer will require 3-1/4" depth for installation. Due to the extra thickness of the panel and box that the potentiometer shaft has to go through, the shaft should be ordered 1/2" longer than usual and then cut at the right point.

As per my discussion with Alex, I am enclosing eight stamped, self-addressed envelopes for the next eight issues of MELLONMR.

Sincerely yours,

James E. LuValle
Director of Basic Research

JEL:mls

Enclosures

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

DEPARTAMENTO DE FISICA
PERU 222 - BUENOS AIRES
ARGENTINA

Professor V. J. Kowalewski

BUENOS AIRES, March 13th. 1962.-

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
Pittsburgh 13. Pa.   "Long Range Interaction in Benzaldehydes"

Dear Dr. Bother-By:

Since a long time ago we have been puzzled by the fact that in the spectra of some benzaldehydes the signal due to the aldehydic proton appears as a fine doublet while in others as a singlet. A splitting of the signal could only be ascribed to a coupling with a ring proton, but a search for similar splitting in the spectrum of the ring protons was fruitless because the ring lines were rather broad.

A statistical survey made upon all commercially available substituted benzaldehydes showed that a splitting could be observed only when: 1) the ring proton in position 2 was substituted, and 2) when the proton in position 5 was not substituted.

At last the problem was solved trying different solvents. In the case of 2,4 dichloro and 2,4 dimethoxibenzaldehydes the signal due to proton Nr. 5 appears split into eight lines, while proton 6 remains unaffected.

The rules which follow from the above would be quite simple were it not for the 2,4 dihydroxibenzaldehyde, the spectrum of which substance point to proton 3 as responsible of the aldehydic splitting.
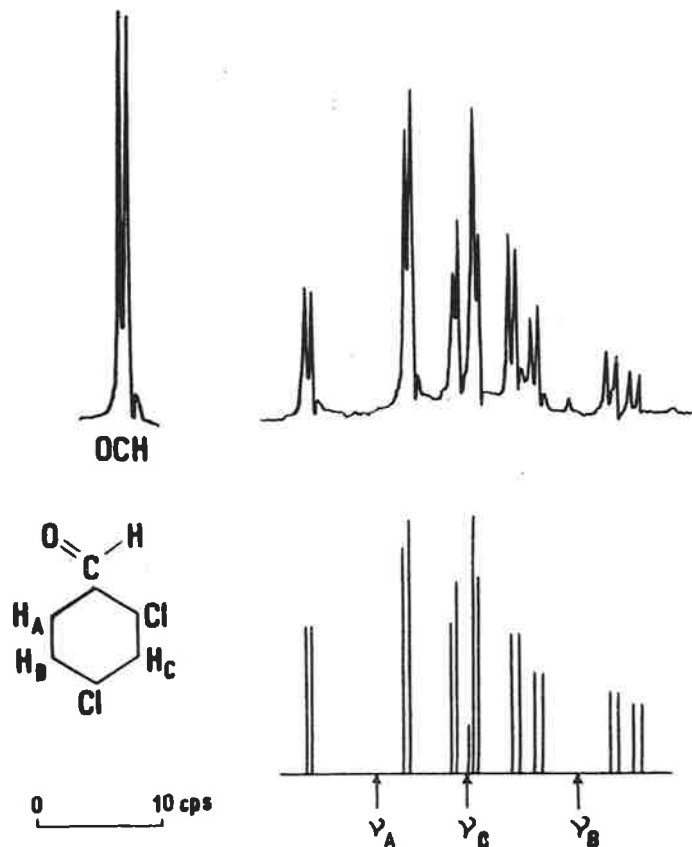
Accompanied is the spectrum of 2,4 dichlorobenzaldehyde, together with the calculated one by our Mercury Ferranti computer using an ABC iterative program. A full description will appear in the Journal of Chemical Physics.

Yours sincerely,

Valdemar J. Kowalewski

Dora G. de Kowalewski

INSTITUT FÜR ANORGANISCHE CHEMIE

DER

UNIVERSITÄT MÜNCHEN

MÜNCHEN 2, den 8.3.1962

MEISERSTR. 1
FERNSPRECHER 55 79 76

Dr. Aksel A. Bothner-By,
Director of Research,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.

U. S. A.

Dear Dr. Bothner-By,

     thank you very much for your kind letter and the latest
modification of your program. We already contacted the German IBM
branch and hope to finish our calculation of the butadiene spectrum
in metal complexes rather soon. Also let me thank you really very
much for the two issues of MELLONMR. We certainly would appreciate
it greatly, if you would put our adress on the mailing list. Of
course, we shall contribute to the contents. Our main concern is,
however, not to be able to send such valuable letters as other
well-experienced members of the "MELLONMR club".

     At the present time we are engaged in mostly routine ana-
lyses of metal organic complexes, containing olefins, cyclobutadiene,
cyclopentadiene, benzene etc. as ligands. For some of these compounds
we try to calculate the theoretical spectra. In the near future
a report on the efforts should be possible.

     In order to make our Varian-A-60 more versatile we added
a small and unsophisticated extra (on advice of Mr. Tschudin of
the Zürich Varian field office), cf. drawing. By means of this
addition, our sweep width can be extended up to 2000 cps on the
high-field side of tetramethylsilane. This range is important, as
you will know, for the analysis of protons directly bound to
transition metals.

     At the positions II, III and IV of the switch the off-set
can be set at - 1000, - 1500 and - 2000 cps, using the A-60 termino-
logy.

TB 902, 7 ←

TB 901, 3 ←

R1=2.5 k , 1W
R2=3.5 k , 1W
R3=5 k , 1W
R4=21 k , 5W
R5=28 k , 3W
R6=40 k , 2W

With best compliments I remain,

Sincerely yours,

Heinz Fritz

Heinz P. Fritz

UNION CARBIDE PLASTICS COMPANY

DIVISION OF UNION CARBIDE CORPORATION

RIVER ROAD, BOUND BROOK, N. J.

March 12, 1962

Dr. Barry L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 18, Pa.

Dear Barry,

     As my first contribution to Mellon NMR, I wish to
report certain items concerning the installation of our A-60 spec-
trometer which may be of general interest.

     Since our line voltage was far too low (less than 190
V.A.C. and fluctuating) to allow direct operation of the spectrometer,
we purchased a Sorensen 5000-2S line voltage regulator. It has
worked well with our installation. With a minimum of trouble, we
have exceeded the Varian specifications. I am led to comment on
this matter by the many reports of trouble with the Sorensen regu-
lator. But perhaps I am missing some of the less obvious malfunc-
tions which accompany the use of this regulator. The criterion on
which its performance was judged is simply the improvement in per-
formance of the spectrometer.

     I understand that some people are interested in building
a recirculating system for the magnet cooling water of an A-60 spec-
trometer. For those people, perhaps the following will be of interest.
We have built such a system for our A-60 unit, and it has been in flaw-
less continuous operation for about three months. The idea for the
system was conceived by Ray Hanselman and developed by Bob Codner,
both of whom are of these laboratories. Drawings of the system are
enclosed with this letter.

     Deionized water from the 12 gallon tank is circulated
through a Ross heat exchanger (which is cooled by city water) and the
magnet coils, and then returned to the reservoir. If the solenoid
entrance valve to the magnet should close, the pressure relief valve
will never allow pressures within the system to exceed a preset valve,
which in our case is 45 p.s.i. In order to protect the solenoid valves
in the magnet from the pulsations of the gear pump, a water hammer
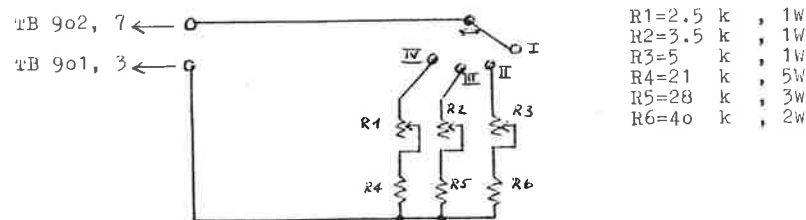
eliminator was attached to the line which connects to the magnet inlet. In an effort to keep down the operating noise level, the components were mounted on the tank lid over a 1/4" piece of rubber. The vital parts for the system may be obtained as follows:

Tank Price $75.50. Obtained from Metal Products Corp., 41-47 W. 19th St., Weehawken, N.J.

Heat Exchanger Price $33.13. Ross, size 200-8, single pass, baffle spacing D-1 Model 7M-200-8-D1. Obtained from American Standard Ind. Div., 1060 Broad St., Newark, N.J.

Pump & Motor Price $93.95. Eco pump, brass model 121T, close coupled 1/4" H.P. motor, 1750 RPM, 1 phase, 60 , 110V. Obtained from Eco Engineering Co., 12 New York Ave., Newark, N.J.

Water Hammer Eliminator #POW, 1/2" size for 1/2" pipe, 6 1/2" high. Obtained from McMaster-Carr Co. Price $9.00.
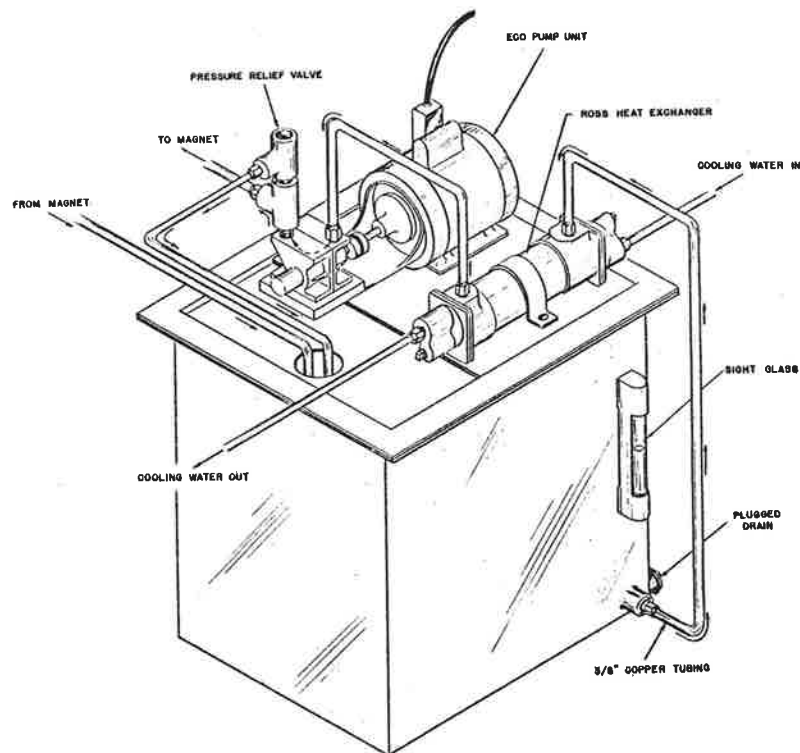
Naturally, the above list is only to serve as a guide. A glance at the list will convince one that the cost of building such a system is not too much greater than two hundred dollars, excluding labor. Should anyone have an interest in building this recirculator and find the information contained here insufficient, I will be very happy to discuss the matter further on a private basis.

Very truly yours,

Bill.

William F. Beach

WFB:hlk

10"

18"

ROLLED EDGE OR
1/2" FLANGE

16 GAGE STAINLESS STEEL
TANK

14"

1/2" S.S PIPE COUPLING
FOR DRAIN
WELD IN PLACE

2"

2"

19"

1"

.5"

12 GAGE STAINLESS STEEL
TOP FOR TANK

17"

W. F. Beach, Union Carbide

Division of Physical Chemistry
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

Cable address: Technology
Research Group
for Nuclear Magnetic Resonance

LOA,EF/BR

Stockholm, March 16, 1962.

Dr. A.A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13 Pa.

U S A

Dear Dr. Bothner-By,

In a study of the anisotropy of the I^{127} resonance in deformed KI single crystals first reported by Otsuka[1] we had difficulties in computing the first moment of the NMR signal as the largest contributions to the moment come from the long tails of the resonance where the signal-to-noise factor is low. These tails are not mentioned by Otsuka (they almost disappear in highly deformed crystals) but have been observed by Briscoe and Squire[2], Solomon[3] and Hon & Bray[4]. Observation in our laboratory of the tails at highest possible amplification revealed a structure in them. A resonance spectrum (the derivative) is shown in fig. 1 where the main resonance has been attenuated 30 times.

Further investigation showed that the distance of these unexpected peaks from the main resonance peak is inversely proportional to the main peak resonance frequency. (To prove this we made use of the device described in Mellon NMR No. 39 by G.W. Smith. Thank you!) They can accordingly be ascribed to second order quadrupole effects.

Quenching and deformation experiments seem to show that the tails themselves are first order effects (satellites), since they diminish with increasing dislocation density, while the peaks remain in their initial positions. The angular dependence of the tail amplitude is consistent with the observations by Hon and Bray on first order effects in NaI crystals.
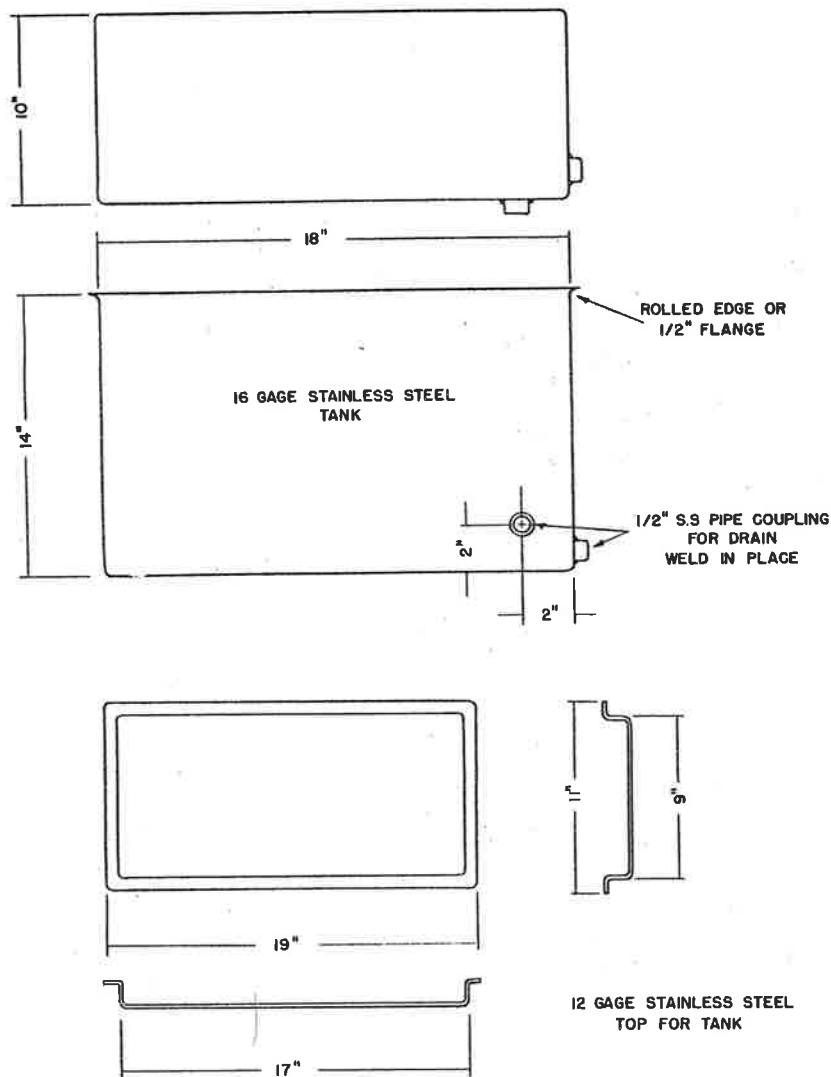
The extra peaks are believed to be the resonances of iodine ions in the neighbourhood of impurity ions (probably Na and/or Cl) in lattice positions. The peaks change their shapes and positions considerably when the crystal is rotated in the magnetic field, indicating a pronounced anisotropy of the iodine polarizations due to the presumed impurity point disturbance.

Pending a quantitative sample impurity analysis, we are now making preparations for a theoretical investigation of the proposed explanation of the extra peaks.

Yours sincerely,

L.-O. Andersson   Erik Forslind

References:

1. E. Otsuka, J.Phys.Soc.Japan 13, 1155 (1958)
2. C.V. Briscoe, C.F. Squire, Phys.Rev. 112, 1540 (1958)
3. I. Solomon, Phys.Rev. 110, 61 (1957)
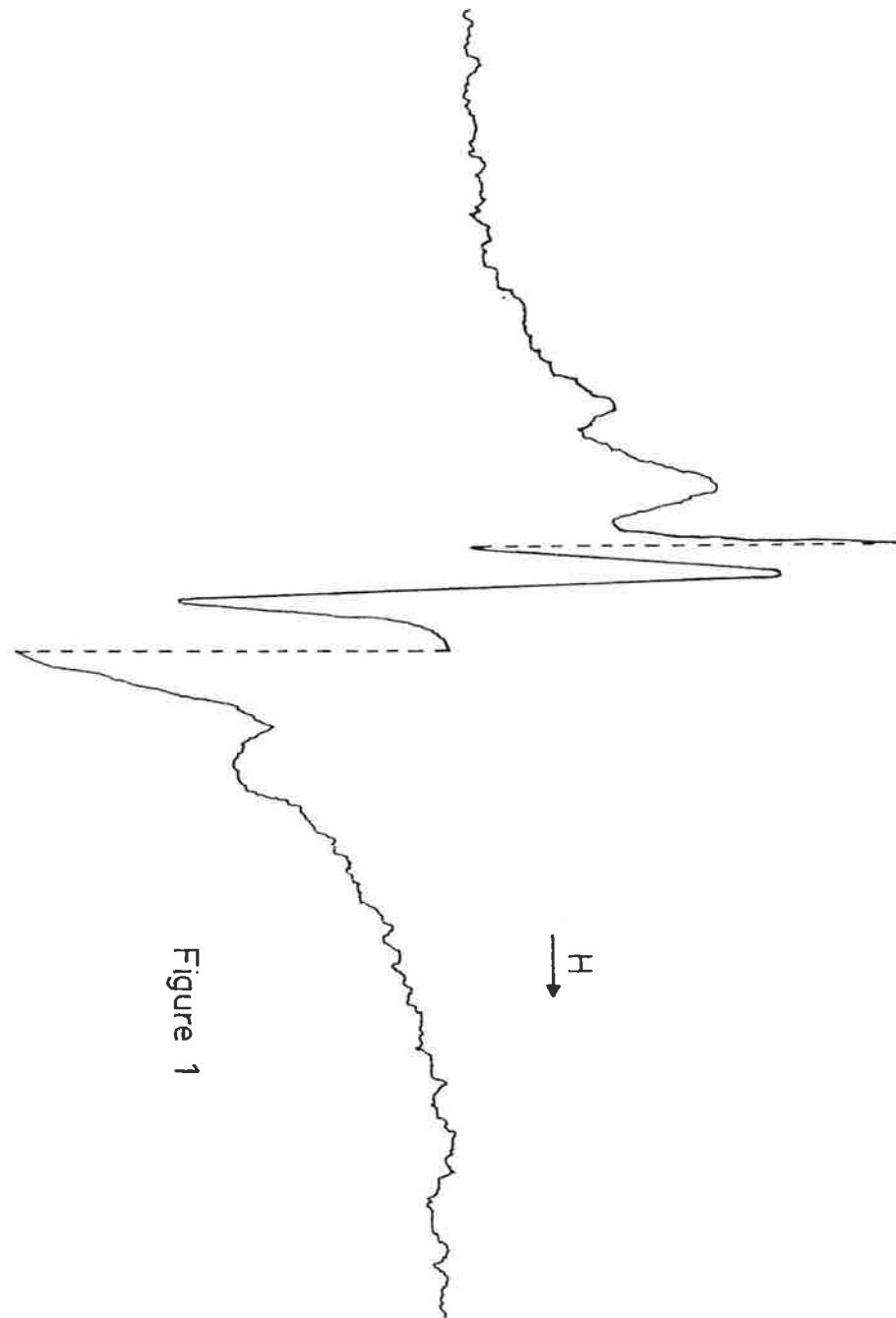4. J.F. Hon, P.J. Bray, J.Appl.Phys. 30, 1425 (1959)

Figure 1

Division of Physical Chemistry

THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70

SWEDEN

Cable address: Technology

EF,MSB/BR

Stockholm, February 2, 1962.

Dr. A.A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

U S A

Dear Dr. Bothner-By,

We wish to report some internal standard effects and water lattice distorsions in a PMR study of aqueous solutions of the alkali halides. Molal shifts in such solutions have previously been determined amongst others by Hertz and Spalthoff (Z. Elchem. 63, 1096 (1959)), who used internal referencing with t-butanol. Since one can never be quite sure to avoid medium effects in all such cases we preferred to apply the external standard method and susceptibility corrections to the measured shifts. The Wilmad Glass Co. coaxial precision bore glass tubes have been found most suitable for the purpose. Density and molecular susceptibility data available in the literature have been used in addition to measurements performed here to calculate the volume susceptibilities of the solutions. The NMR measurements have been made with a Varian 40 Mc/sec equipment.

The molal shifts, defined as $\left[\dfrac{H - H_{ref}}{H_{ref}} - \dfrac{2\pi}{3}(k - k_{ref}) \right] \cdot 10^8$

for external referencing show a remarkably good consistency excepting the cases of RbI and CsI, as can be seen in Table I.

Table I.

Salt	$\delta \pm \epsilon$ a)	δ b) H&S
LiCl	1.7 ± 0.3	2.2 ± 0.5
LiBr	3.1 ± 0.3	
LiI	8.8 ± 0.3	
NaF	$- 3.6 \pm 0.3$	$- 2.5 \pm 1$
NaCl	8.6 ± 0.3	8.8 ± 0.5
NaBr	11.9 ± 0.3	11.3 ± 0.5
NaI	13.2 ± 0.3	15.0 ± 0.5
KF	$- 2.2 \pm 0.3$	$- 2.5 \pm 0.5$
KCl	9.9 ± 0.3	8.8 ± 0.5
KBr	12.3 ± 0.3	11.3 ± 0.5
KI	15.0 ± 0.3	15.0 ± 0.5
RbF	$- 2.4 \pm 0.3$	
RbCl	7.5 ± 0.3	
RbBr	12.3 ± 0.3	
RbI	11.5 ± 0.3	15.0 ± 0.5
CsF	$- 5.3 \pm 0.3$	
CsCl	5.9 ± 0.3	
CsBr	8.6 ± 0.3	
CsI	9.5 ± 0.4	14.6 ± 0.5
$NaClO_4$	13.2 ± 0.3	

a) ϵ is the estimated uncertainty in δ; ϵ is the standard deviation of the shift due to errors in the frequency readings and susceptibility corrections.

b) Molal shifts, determined by Herz and Spalthoff, using internal standard.

In order to check these deviations we have redetermined the molal shifts for the two salts, using a t-butanol internal standard according to Hertz and Spalthoff. Their results were confirmed and, barring errors of quite improbable magnitude in the susceptibility determinations, the observed difference between the internal and external standard methods was thus established. It appears that the combined steric effects of the large cations in question, and t-butanol molecules are responsible for the upfield shifts and the deviation from the simple law of addidivity in the low
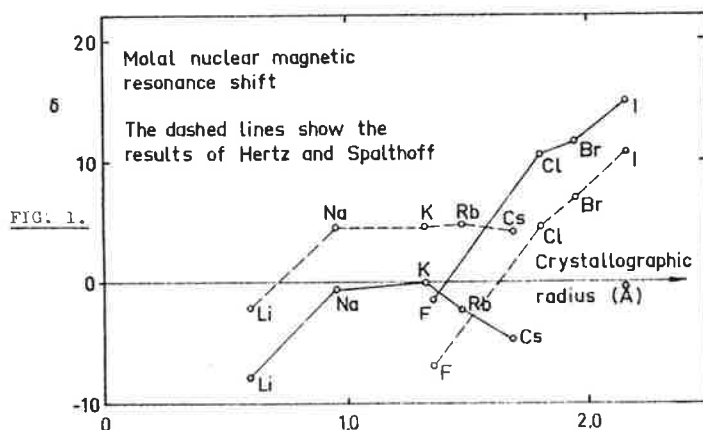
concentration range. It seems desirable to repeat and extend these observations regarding the structural effects of internal reference substances.

We have also, with some success, attempted a model to resolve the molal shifts into ionic contributions, assuming the validity of current ideas regarding water lattice distorsions and bond polarization effects due to the solute ions. The first effect is assumed to be proportional to the ionic volume, while the second is taken proportional to the atomic dipole moment which is created when the ion, interacting with the water lattice, leaves its ground state under the formation of bonding hybrid orbitals. The results obtained are summarized in Fig. 1, including a comparison with the values of Hertz and Spalthoff.

Yours sincerely

M.S. Bergqvist

E. Forslind

FIG. 1.

Molal nuclear magnetic resonance shift

The dashed lines show the results of Hertz and Spalthoff

Crystallographic radius (Å)

The Standard Oil Company
(An Ohio Corporation)
Research Department
4440 Warrensville Center Road
Cleveland 28, Ohio

E C HUGHES
VICE PRESIDENT

March 5, 1962.

Dr. B. Shapiro
Mellon Institute
Pittsburgh, Pa.

Dear Barry:

We would like to recommend an ink that is virtually non-clogging and fast drying for use in all types of Varian recorders. Besides being jet black, it is also water soluble and therefore quite easy to clean when necessary.

This ink can be ordered from General Electric in West Lynn, Massachusetts. Please request that they send you, "Fast Drying Recorder Ink, Black, Spec. No. D50W79A."

The use of this ink should undoubtedly eliminate all problems pertaining to inks that were voiced at the last NMR conference in Pittsburgh.

Sincerely yours,

THE STANDARD OIL COMPANY (OHIO)

Bill Ritchey

Herbert Grossman

Further Comments on the Above Ink

1. Through the kindness of Herb and Bill who provided us with a sample, we have tried this ink and have also found it very satisfactory. It has virtually eliminated the tedious and expensive cleaning and discarding of A-60 pens.

2. The color is, in our opinion, not "jet black" but has a slight gray-blue-purple cast. While it is not as esthetically pleasing (to us) as the K & E 3015, it is easy on the eye. Even more important, it reproduces well, at least by the Xerox process.

3. General Electric has a $12 minimum order, so there is very little point in ordering only a few ounces of this ink. This minimum order amount is good for 24 ounces of this excellent ink.

B. L. Shapiro
Mellon Institute

1. <u>Policy</u>: Not since Issue #1 (nearly four years ago) has a statement of aims and policy appeared in MELLONMR. The list of participants has grown mightily since then, and it would seem about time to reexamine publicly the function of MELLONMR.

MELLONMR is first and foremost a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of editorial policy is "We print anything." (This is usually followed by the mental reservation, "that won't land us in jail"). In Issue #1, we suggested as possible subjects:

  1. Reproductions of spectra or parts of spectra
  2. Measurements and calculations on same
  3. Theoretical considerations and interpretations
  4. Novel experimental methods and techniques
  5. Complete or partial mysteries
  6. Comments on material appearing in earlier letters
  7. Requests for help in locating odd or rare compounds.

Most contributions have in fact contained material classifiable under 1,2,3 and/or 4. On rare occasions 5 or 6 have turned up. We can't help feeling that there are plenty of missed opportunities for communication: for example announcements of forthcoming meetings, colloquia, symposia, books and such all, or notice of availability of post-doctoral positions, or readiness to accept same. We had a "preprints available" section for a while, but this withered and fell off the vine for lack of cultivation. You're the boss. You can surely think of things you would like people to know, or would like to know yourself, which we haven't thought of.

Foreign participants ought not to feel obliged to render their contributions in English.

2. <u>Bibliography</u>: Included in this issue are titles of a number of articles kindly brought to our attention by Dr. Stothers. Conclusive proof that we do miss numbers of references in our bibliography, unfortunately. We urge you, if you catch others which we have missed, to let us know, or better yet, send in supplementary sheets of this kind.

3. <u>Subscriptions</u>: Reassessment of costs and resources have convinced us that we can still expand the mailing list a little, covering the costs ourselves. Jim LuValle's letter notwithstanding, it is not necessary to send self-addressed stamped envelopes with your contribution (though if you feel overpoweringly impelled to do so, we will, of course, use them). We do appreciate receiving 200 copies (increased circulation!) of your contributions if it is convenient for you. If it is not, don't worry.

<u>Participation</u> was and is the prime requisite for receiving the letters. We feel we have to be ruthless in this connection, and are instituting a new schedule. Seven months after your last contribution you will receive a "reminder letter." If no contribution is then forthcoming nine months after your last contribution you will receive the "ultimatum letter." One contribution thus covers 9 issues. If you are dropped from the mailing list, you can be reinstated by sending in a contribution, and you will receive back issues and forthcoming issues at the rate of 9/contribution.

4. <u>Brevity</u>: Brevity is good.

5. <u>Public Quotation</u>: Public quotation is not good. Reference to MELLONMR in the scientific literature is definitely awful. Reproduction of material from MELLONMR is a ticklish matter on which you should consult your conscience, keeping in mind that the author has probably not released his material to the public at large as yet.

6. <u>Suggestions</u>: We welcome them.

A. A. B. and B. L. S.