THE
NMR
NEWSLETTER

No. 514

July 2001

NUTS puts *you* in control of your NMR data

Edit individual slices to remove artifacts or reduce t_1 noise
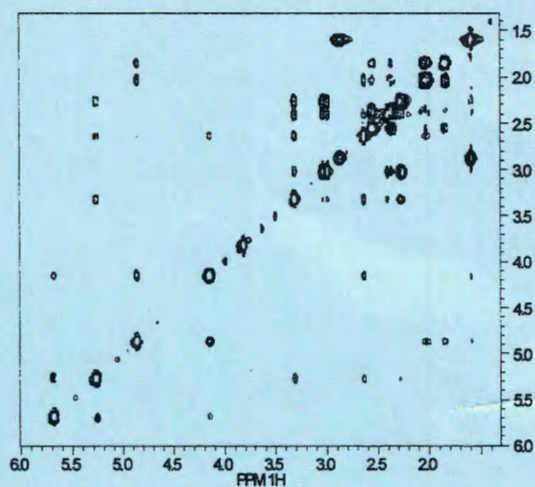
NOESY spectrum of codeine, same contour threshold, before and after editing

1
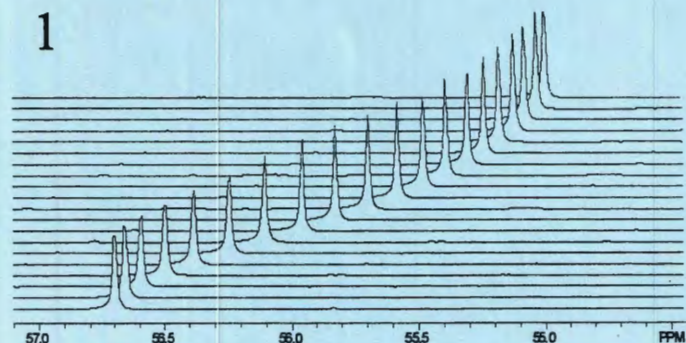
Field shift (**1**) during block-averaged data acquisition. Each slice must be correctly referenced to align peaks (**2**), then summed to give the desired final spectrum (**3**).

2

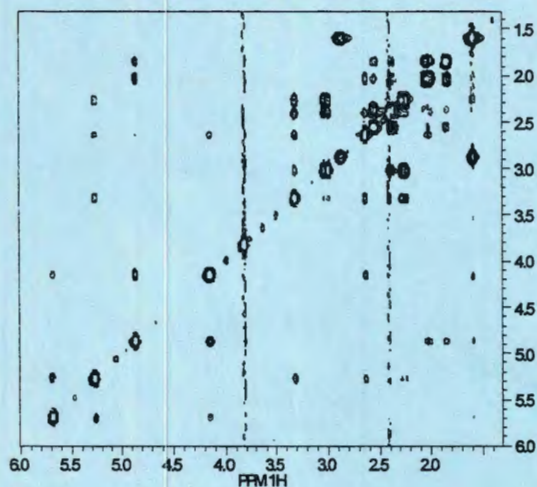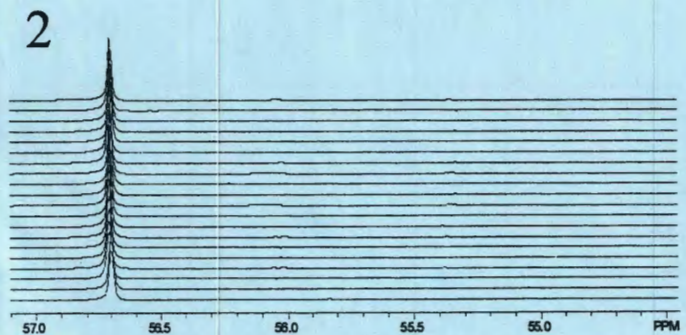**3** NUTS aligns and sums data with a single command, eliminating tedious manual adjustments.

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SPONSORS OF *THE NMR NEWSLETTER*

FORTHCOMING NMR MEETINGS

ESR and Solid State NMR in High Magnetic Fields, University Stuttgart, Germany, **July 22-26, 2001**. Contact: Prof. Hans Paus, 2 Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany. Tel: ++49-711-685-5223; Fax: ++40-711-685-5282; E-mail: ampere2001@physik.uni-stuttgart.de.

43rd Rocky Mountain Conference on Analytical Chemistry, Denver Marriott City Center, Denver, CO, **July 29-August 2, 2001**. Email: milestone@bod.net. Web: www.milestoneshows.com/rmcac.

ISMAR 2001, *Note change of meeting location:* Convention Center of Rodos Palace Hotel in Rhodes, Greece. **August 19-24, 2001**; See http://www.tau.ac.il/chemistry/ISMAR.html.
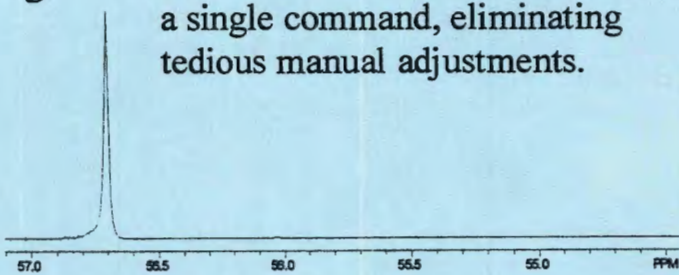
Sixth International Conference on Magnetic Resonance Microscopy, Nottingham, UK, **September 2-5, 2001**. http://www.magres.nottingham.ac.uk/conferences/2001/icmrm.

14th European Symposium on Polymer Spectroscopy, Dreikönigskirche – Haus der Kirche, Dresden, Germany, **September 2-5, 2001**. Contact: Institut für Polymerforschung Dresden c. V., ESOPS 14, Postfach 12 04 11, 01005 Dresden, Germany. Tel: +49 351 4658-282; Fax: +49 351-4658-214; E-mail: espos@ipfdd.de.

Fourth International Conference on Molecular Structural Biology, Vienna, Austria, **September 5-9, 2001**. Contact: Dr. Andreas Kungl, Austrian Chemical Society (GÖCH), Biochemistry Subgroup, c/0 Institute of Pharmaceutical Chemistry, Univeristy of Graz, Universitätsplatz 1, A-8010 Graz, Austria. Tel: +43 316 380 5373; Faz: +43 316 382541; E-mail: andreas.kungl@kfunigraz.ac.at.

2nd Alpine Conference on Solid-State NMR, Chamonix-Mont Blanc, France, **September 9-13, 2001**; Contact: Alpine Conference Secretariat, Laboratoire STIM, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 7, France; alpine.SSNMR@ens-lyon.fr; Tel. +33-(0)4 72-72-84-86/ 83 84; Fax. +33 (0)4 72 72 84 83; http://www.ens-lyon.fr/STIM/alpineweb/html.

EMBO Practical Course: Structure Determination of Biological Macromolecules by Solution NMR, EMBL, Meyerhofstr. l, D-69117 Heidelberg, Germany, **September 12-19, 2001**; Email: nilges@EMBL-Heidelberg.de; sattler@EMBL-Heidelberg.de; http://www.embl-heidelberg.de/nmr/sattler/embo.

EMBO Workshop on NMR and Molecular Recognition, Ravello, Italy, **October 3-7, 2001**; Contact: Dr. T. Tancredi: ttancredi@icmib.na.cnr.it, or Dr. P. Amodeo: pamodeo@icmib.na.cnr.it. Information: http://www3.icmib.na.cnr.it/ravello2001.

43rd ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, CA, **April 14-19, 2002.** More information will be posted when available

XXth International Conference on Magnetic Resonance in Biological Systems, Toronto, Ont., **August 25-30, 2002.** For further information check www.uso.ca/chem/icmrbs/, or contact: mgordon@julian.uso.ca.

Department of Radiology
The Mary Nell and Ralph B. Rogers
Magnetic Resonance Center

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

May 31, 2001

(received 6/5/2001)

^{23}Na NMR Relaxation in Aqueous Systems

Dear Barry,

In preparing my upcoming paper[1] on ^{23}Na NMR relaxation in aqueous heterogeneous systems, I ran into an interesting, simple correlation for aqueous solutions of NaCl. Let me explain.

Recall that the NMR line shape and relaxation times of spin 3/2 nuclei such as ^{23}Na are determined mainly by the interaction between the nuclear electric quadrupole moment eQ and the electric field gradients at the nucleus. The electric field gradients are given by the second spatial derivatives of the electrostatic potential that are determined by the distribution of electric charges and electric dipole moments in the vicinity of the nucleus. Molecular and atomic motions cause fluctuations in this distribution. The electric field gradient (efg) from an axially symmetric charge distribution, such as that due to a single electric charge e, is characterized by its principal value eq. The effect of eq on the quadrupole interaction depends on the polar and azimuthal angles θ and ϕ that describe the orientation of eq in the magnetic field $\mathbf{B}_0$ of the NMR spectrometer.

Aqueous solutions contain charged ions (Cl$^-$ and Na$^+$) and water molecules that have electric dipole moments. The value of $eq(t)$ at a ^{23}Na nucleus due to one ionic charge e that is moving randomly is

$$eq(t) = 2e/[r(t)]^3$$

where $r(t)$ is the instantaneous distance between the ionic charge and the nucleus, and $\theta(t)$ and $\phi(t)$ are the instantaneous polar and azimuthal angles in $\mathbf{B}_0$ of the vector joining the nucleus and the ionic charge.

The value from a point electric dipole moment μ of a water molecule that is moving randomly is

$$eq(t) = 6\mu/[r(t)]^4$$

where $r(t)$ is the instantaneous distance between the point electric dipole and the nucleus and $\theta(t)$ and $\phi(t)$ are the instantaneous polar and azimuthal angles of the angle between the dipole moment vector and $\mathbf{B}_0$.

Of course, we commonly assume that the correlation times that describe the $eq(t)$ fluctuations are scaled by the viscosity.

Also recall that the motions in dilute solutions of simple electrolytes are rapid, similar to the motions in pure water, and that the viscosity of NaCl solutions increases only slightly with increasing concentration. Consequently the τ_c is similar to that of water (in the range of 3 - 10 ps) and $\tau_c \ll 1/\omega_0$.

Values of $R_1 = 1/T_1$ measured (by Dr. Pi-Yu Zhao here at the Rogers Center) at 21 °C for NaCl concentrations from 0.10 to 5.00 molal are shown in Fig. 1. The R_1 values increase only about 50% over this concentration range even though the concentration is increased 50-fold. This small increase, together with the large extrapolated value of $R_1 = 18.5$ s^{-1} at zero concentration, indicates that the contributions of efg's from the sodium and chloride ions to the relaxation are small compared to those from the electric dipole moments of the water molecules. This tentative conclusion is supported by making the following corrections to the R_1 values.

An increase in viscosity slows the motions in liquids and increases τ_c. Making the adjustment $R_{1,v} = R_1/\eta_{rel}$, where η_{rel} is the viscosity of the solution compared to the viscosity of pure water should correct for this viscosity effect. Figure 1 shows that this correction actually results in a decrease in relaxation rate. However, the increase in NaCl concentration also results in a decrease in the number of water molecules in a cubic centimeter of solution, decreasing the number of electric dipole moments. The further adjustment $R_{1,v,f} = R_{1,v}/f$, where f is the fraction of solution volume that is occupied by water molecules, should correct for this effect. Figure 1 shows that $R_{1,v,f}$ is indeed independent of concentration (within experimental error).

The strength of the quadrupole interaction can be roughly approximated by using a "reasonable" estimate of τ_c. If we assume that $\tau_c = 4$ ps, then use of basic relaxation relationships with $R_1 = 18.5$ sec^{-1} yields an effective QCC = 1.1 MHz.

Any constructive comments would be appreciated.

Sincerely,

Don

Donald E. Woessner
donald.woessner@utsouthwestern.edu

Figure 1. Measured and corrected ^{23}Na NMR spin-lattice relaxation rate in aqueous NaCl solutions at 21 °C as a function of NaCl concentration in molality. (a) R_1, (b) $R_{1,v} = R_1/\eta_{rel}$, (c) $R_{1,v,f} = R_{1,v}/f$. Smooth line (a) is a second-order polynomial fit; smooth line (b) is a first-order polynomial fit; and smooth line (c) is a zero'th-order polynomial fit.

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[1] Woessner DE. NMR relaxation of spin 3/2 nuclei: Effects of structure, order, and dynamics in aqueous heterogeneous systems. Concepts Magn Reson 2001; 13: in press.
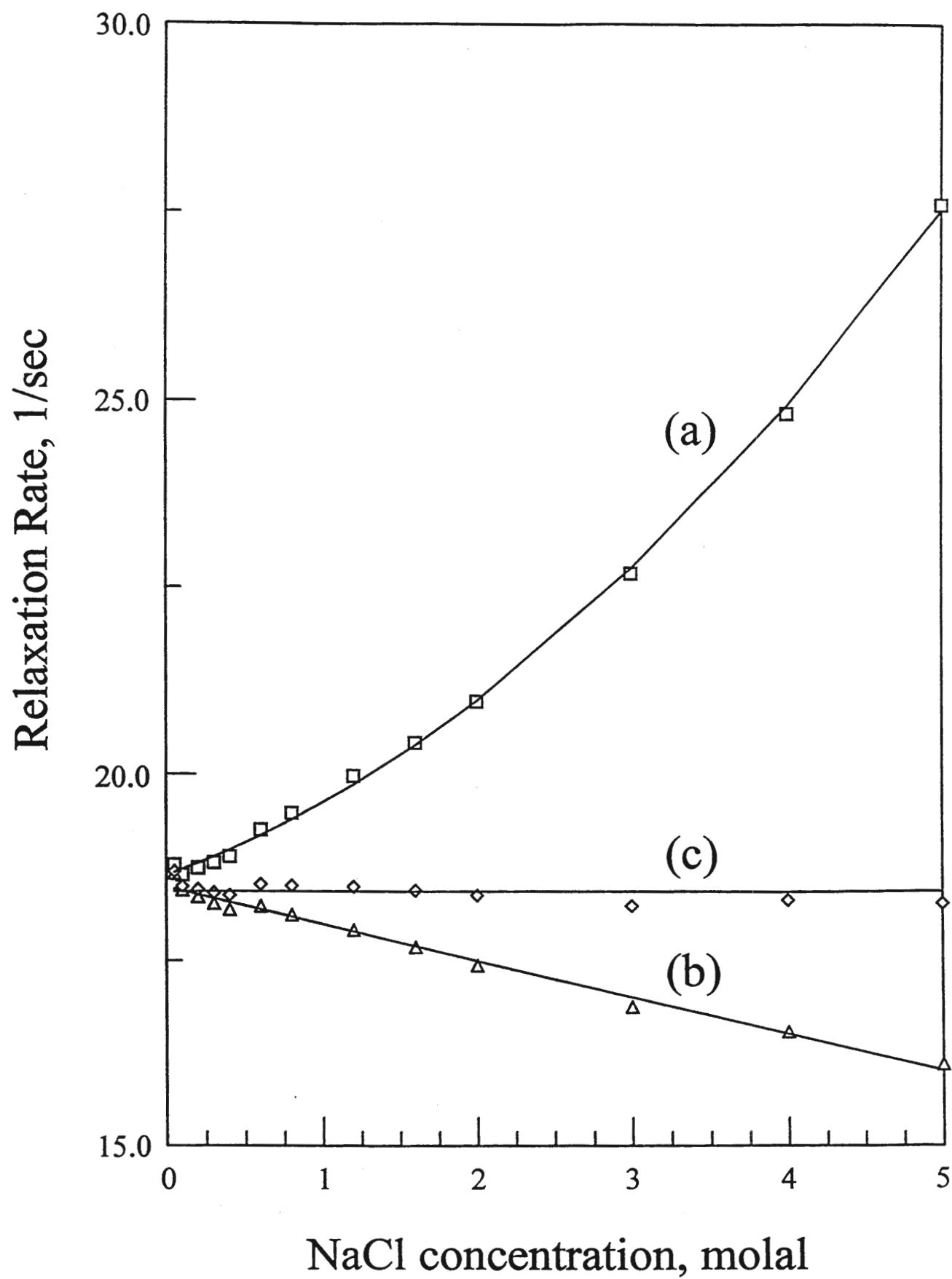
Figure 1.

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Overview

Bruker's 900MHz magnet is based on the innovative UltraStabilized™ magnet technology, which is Bruker's proprietary sub-cooled technology for Ultra-High Field NMR operating at 2K. The UltraStabilized™ technology has previously been applied at 750MHz and 800MHz with a proven reliability track record of a large number of systems installed worldwide.

The complete AVANCE 900 UltraStabilized system has been at field and in operation at Bruker's applications laboratory since the end of January 2001.

The achievement of the 900MHz magnet is the result of advanced design technologies, and thorough evaluation of the latest and most advanced superconducting wires, which are required for increased current, forces, and stored energy in this novel magnet. The UltraStabilized™ technology and the success of the 900MHz magnet project are the result of a close collaboration between Bruker and the Research Center Karlsruhe.

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    - ► *Excellent field homogeneity*

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    - ► *Minimal field drift*

900 MHz
800 MHz
20 ppm

Axial Field Plots

- Patented cryostat technology ensures the lowest cryogen evaporation rates for both liquid helium and nitrogen, and therefore minimizes cryogen maintenance and operational costs.
    - ► *Minimal evaporation rates for sub-cooled magnets*

- Advanced technologies enable a compact magnet design that provides:
    - ► *Minimum stray fields for ease of siting*
    - ► *Minimum stored energy for increased safety*

BRUKER BIOSPIN
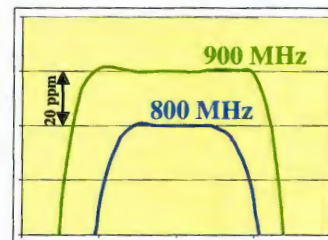
TECHNICAL SPECIFICATIONS

Superconducting Magnet

NMR frequency (^{1}H)	900 MHz
Magnetic field strength	21.2 Tesla
Field stability	< 9 Hz/hr
Superconducting shim coils	z, x, y, z^2, zx, zy, xy, x^2-y^2
Stored energy	< 12MJ
5G Line from the magnetic center - radial distance - axial distance	 < 7.8 m < 9.8 m

Cryostat

Dewar type	UltraStabilized, sub-cooled
Room temperature bore	54 mm
Cryostat height (with magnet stand)	3865 mm
Cryostat diameter	1688 mm
He evaporation rate	< 250 ml/hr
He refill volume	~ 350 liters
Helium hold time	> 60 days
N_2 evaporation rate	< 700 ml/hr
N_2 refill volume	~ 400 liters
N_2 hold time	> 21 days
Magnet stand	included
Vibration dampers	included
Weight (including cryogens)	~ 7000 kg
Minimum ceiling height	< 5300 mm

900 MHz / 54 mm UltraStabilized™ NMR Magnet System
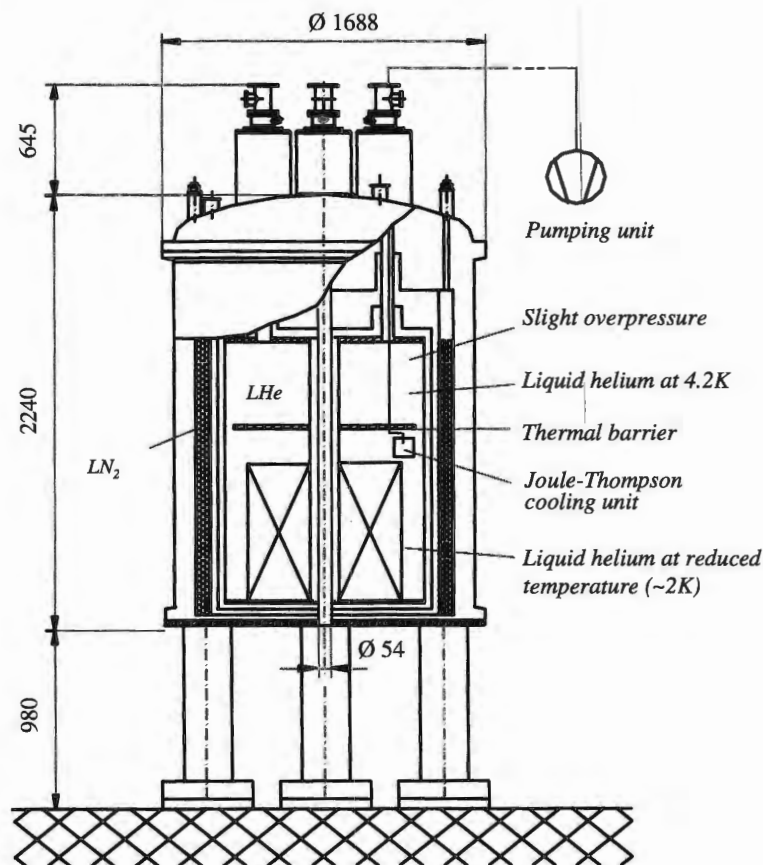
Dimensions in millimeters unless stated otherwise

CE

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Livermore, CA 94550
(925) 456-1020
FAX: (925) 456-1024
info@acornnmr.com

Audio Filters: The Good, the Bad and the Ugly

June 19, 2001

Dear Barry,

(received 6/19/2001)

Audio filters serve to exclude signals at frequencies greater than the spectral width. The ideal filter would have no effect on signals within the spectral window (the "pass-band"), and would eliminate all frequencies outside it (the "stop-band"). A sharp cut-off minimizes the amount of noise that folds back into the spectrum, maximizing the signal to noise ratio. Real filters fall short of this ideal, and can be the source of phase, amplitude and baseline distortions.

The two most common types of filters used in NMR spectrometers are Bessel and the Butterworth. A Butterworth filter yields the flattest amplitude response in the pass-band with a sharp cut-off when entering the stop-band. This gives the best integration, but its slower pulse response time leads to distortions of the first few points in the FID, causing baseline distortions.

A Bessel filter has more amplitude roll-off in the pass-band than a Butterworth filter, meaning that peaks near the edges of the spectral window are attenuated, resulting in inaccurate integration. However, the better pulse response time of the Bessel filter causes less distortion of the early points in the FID and gives flatter baselines.

In addition to the amplitude response in the pass-band and the response time, filters also distort the phase in the pass-band. Bessel and Butterworth filters have typically been used in NMR because these distortions are of low order, and can be corrected with zero- and first-order phase correction. Residual distortions can be observed as slightly out-of-phase peaks near the filter pass-band cut-off (near the ends of the spectrum), usually avoided by widening the spectral width so these distortions do not interfere with peaks of interest.

In the course of providing technical support to NUTS customers, we receive sample data sets whose origins run the gamut of spectrometer models and manufacturers. We have observed spectra with much more severe phase distortions than described above. After phasing with the normal zero- and first-order correction, the remaining out-of-phase peaks are not observed merely at the extreme ends of the spectrum, but well into the spectral window.

In the spectrum of ethylbenzene below, note that the aromatic and methyl peaks are correctly phased, but TMS and methylene peaks have phase distortions of opposite sign. (The spectrum is shown with increased vertical scale so the phase irregularities are clearly visible). It is not possible to phase all peaks simultaneously using zero- and first-order correction. The distortion in this case is approximately 7 degrees, and is clearly sufficient to interfere with integration. Note that both ends of the displayed integral are flat, meaning that the commonly employed "drift and tilt" integral adjustment cannot compensate.
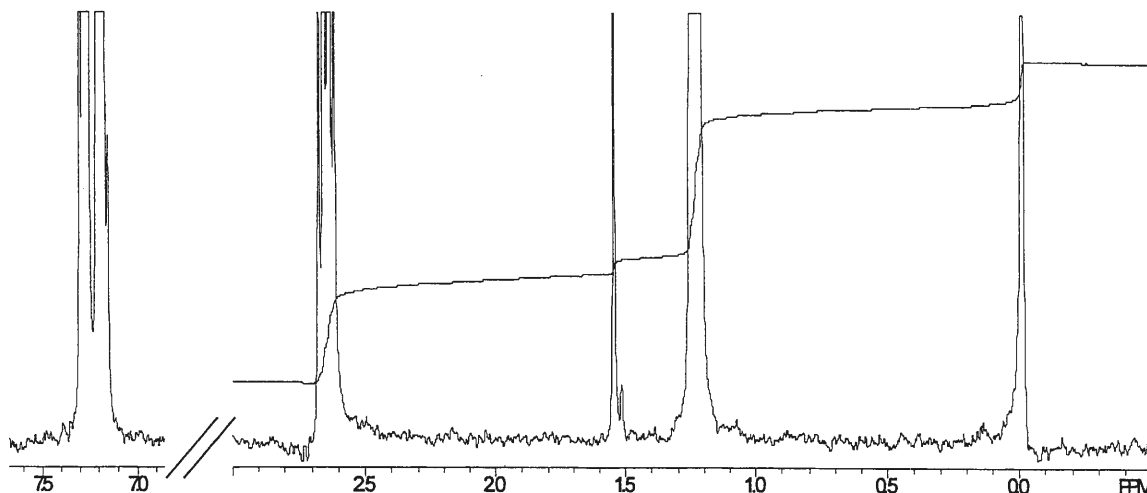
Plots created by processing on the spectrometers often appear correctly phased, leading us to surmise that the spectrometer software is doing something in addition to "traditional" phase correction. The obvious first attempt at resolving this is addition of a second-order term to the phase correction.

The spectrum above resulted from zero- and first-order phase correction of −121 and 37 degrees, respectively. The pivot point is the downfield edge of the spectrum.

The same spectrum is shown below after phase correction using zero-, first- and second-order values of −155, 185 and −130 degrees, respectively. It appears that addition of one more term is sufficient to yield an acceptable spectrum.
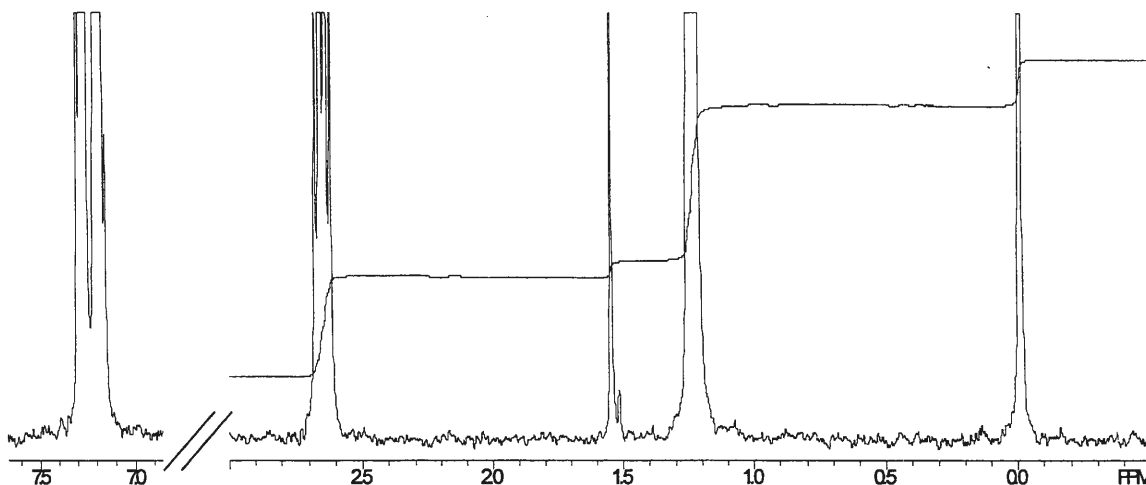
It appears that in the search for ever-increasing signal-to-noise, sharper cut-off filters, which cause undesired phase shifts in the pass-band, are being used. As with many other aspects of NMR hardware, this is a trade-off, and each spectroscopist needs to be aware of the choices being made.

Virginia W. Miner

Woodrow W. Conover

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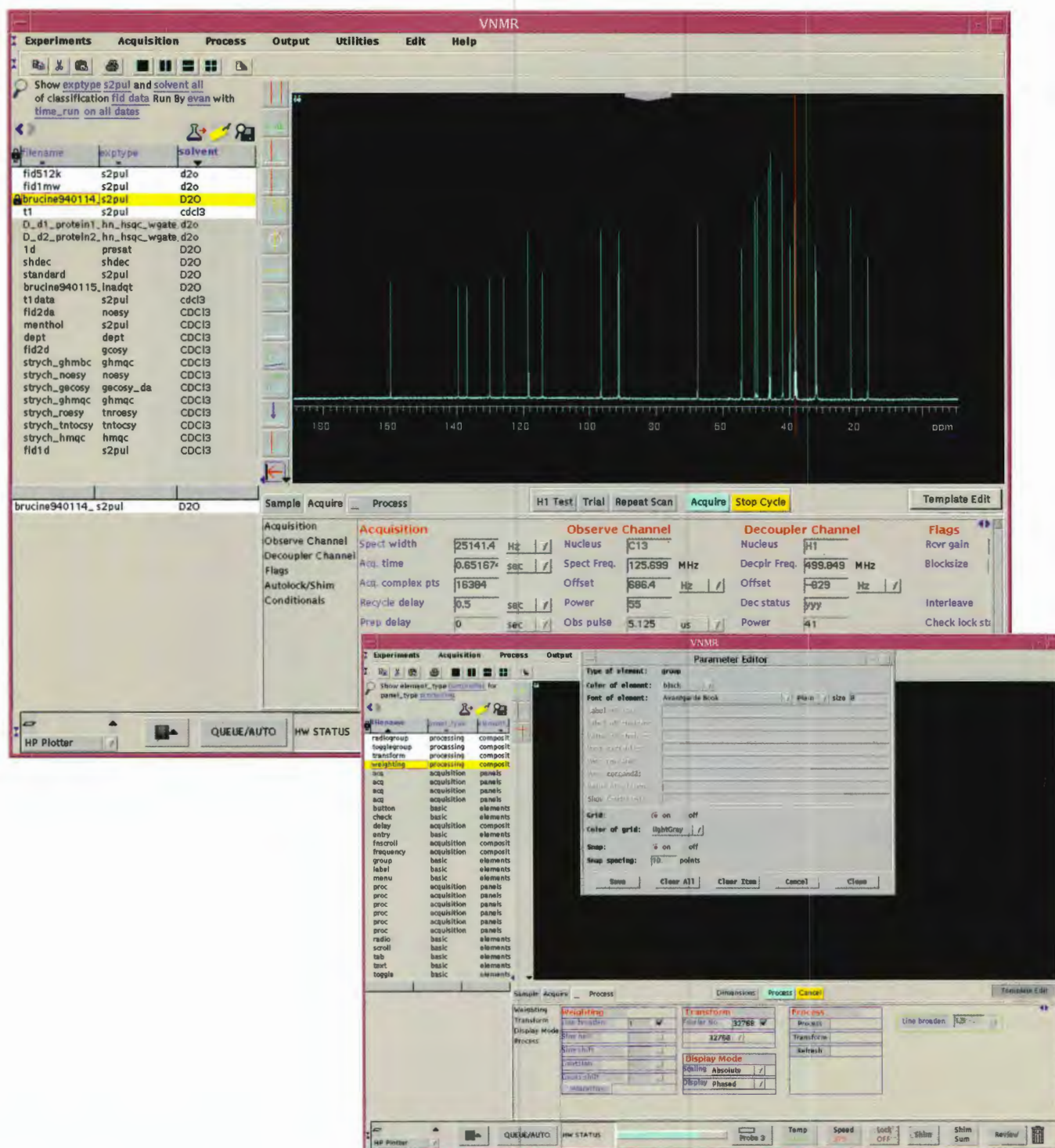
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Princeton, New Jersey 08544-1009

István Pelczer, Ph.D
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Washington Rd.   fax: (609) 258 6746
Princeton, NJ 08544   email: ipelczer@princeton.edu

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Re: Long-range ^2H isotope effect in hydroquinone

06/18/2001

Dear Barry,   (received 6/19/2001)

The following contribution may look like one of those enjoyable recitals from several decades ago, as observation and detailed analysis of isotope effects is nothing new. We would not be surprised if someone had seen already what we present below. However, what we found simply looks beautiful in our eyes; a not well-enough appreciated feature of NMR spectroscopy, which we wish to share with readers of TNN...

In the course of other studies we recorded the ^{13}C spectrum of hydroquinone in highly pure, degassed acetone-d_6 on our Varian Unity/INOVA-600. In such circumstances the water peak can split according to the presence of both ^1H_2O and $^1H^2HO$ and slow exchange (The NMR Newsletter, N° 441., p.2, June 1995). We did see two peaks for the water in the proton spectrum in ca. 3:1 ratio.

A carefully processed high-resolution ^{13}C spectrum showed the following multiple signals for the hydroquinone – the various resonances can be readily assigned to ^2H isotope-shifted species as labeled:
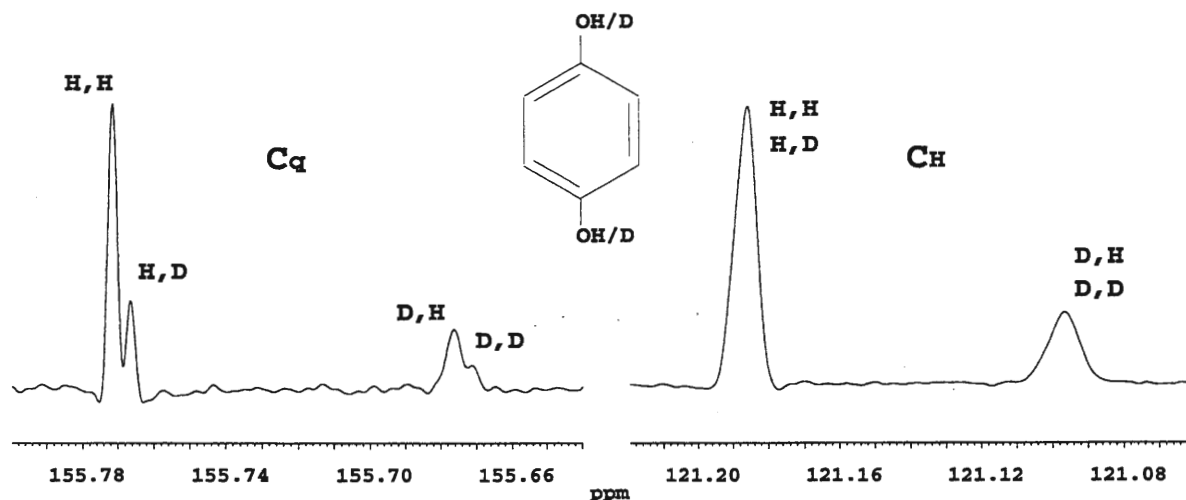
All possible four species can be nicely identified on the C_q signal, and the five-bond ^2H effect on the quaternary carbon is only about 5ppb! The four-bond effect on the protonated carbon remains below the linewidth. (Please note, the scale is not the same for the plots.) If someone could give us reference to similar earlier observation in the same structure, it would be appreciated.

With our best regards,

(István Pelczer)   [traveling on the Far-East]   (Maitland Jones, Jr.)
                              (Alex Bradley)
                         Department of Chemistry
                         Princeton University

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

March 23, 1976

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

"Carbon-13 NMR for the micro-chemist"
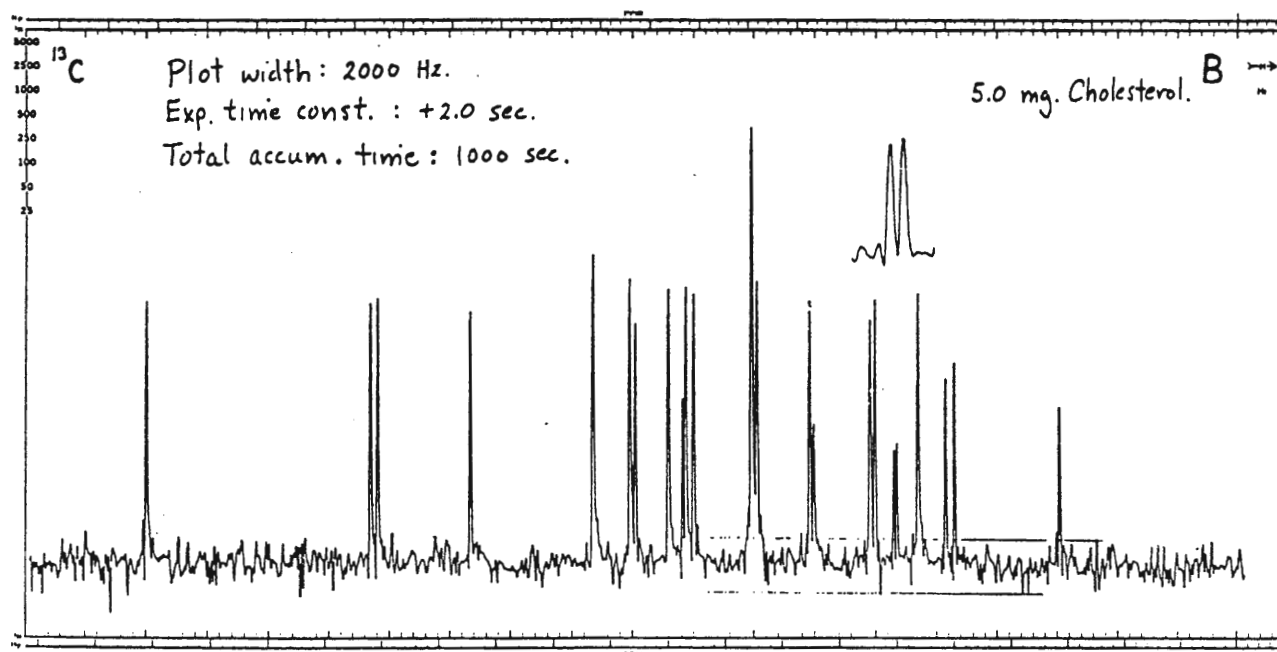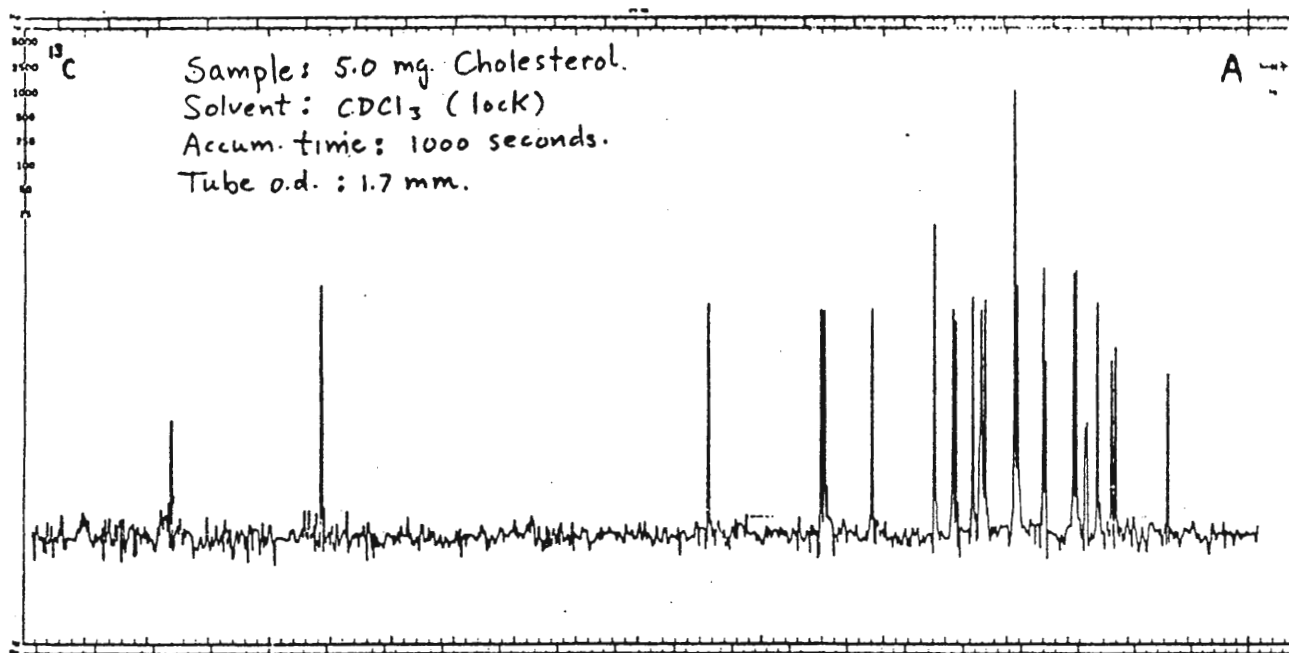
Dear Barry:

Rapid progress in instrumentation is outstripping the spread of information
throughout the community of chemists who could otherwise make better use of
the present capabilities of NMR spectrometers. It may be hard for your
readers to believe that there are still chemists who think that 50 milligrams
is necessary for a decent ^1H spectrum, and a bottle full for a usable ^{13}C
spectrum, but I run into them all too often. While readers of this bulletin
may already be aware of the capabilities described in this letter, they may
not appreciate them enough to participate as fully in the general dissemination
of this information as they might. In hopes of remedying this situation I
offer the following.

For small samples with reasonable solubility in the usual deuterated solvents
there is much to be gained by improving the coupling of the nuclear moments
to the tuned detector circuit. Using an XL-100 spectrometer equipped with a
small coil closely coupled to sample tubes of 1.7 mm o.d., 1.5 mm i.d., we
have obtained the results shown in the attached spectra. Chart A shows the
spectrum of 5 mg of cholesterol obtained in only 1000 seconds. The spectrum
would still be very usable if only 250 seconds were devoted to accumulation
of data. The latter is the scan time that most chemists think of as standard
for a single-scan proton NMR spectrum. Even the most miserly of chemists can
usually spare 5 mg (you get most of it back).

Chart B is a plot expansion that shows that such rapidly-run spectra will tol-
erate some resolution enhancement and resolve completely all of the spectral
lines.

Chart C shows the spectrum of a mixture of fatty acid methyl esters normally
used for GLC calibration. A solution of 3.5 mg in 12 µl of $CDCl_3$ was run for
approx. 15 hrs. with 90° pulses at 6 sec. intervals. The numbers associated
with the peaks are integral intensities, while assignments appear under the
corresponding peaks. Since C_{16}, C_{17}, and C_{18} have more molecular motion, being
at the end of the chain, they have longer T_1's and slightly lower intensities
than C_2, C_3 and the remaining carbon atoms in the chain. The sum of the in-
tensities of the two peaks due to C_{16} was normalized to the intensity of C_2 to
correct for this difference in T_1. Differences in NOE factors were neglected
since essentially full NOE is found for most carbon atoms in these large molecu

Sample: 5.0 mg. Cholesterol.
Solvent: CDCl₃ (lock)
Accum. time: 1000 seconds.
Tube o.d. : 1.7 mm.

A

Plot width: 2000 Hz.
Exp. time const. : +2.0 sec.
Total accum. time: 1000 sec.

5.0 mg. Cholesterol.

B

That the latter assumption is justified is supported by the good agreement of the composition of the sample as determined by NMR with the values on the label. Thus, a 4-component mixture can be quantitatively analyzed by ^{13}C NMR, even if only a few milligrams are available.

Finally, the existence of sub-milligram samples cannot be denied or avoided indefinitely, even by the most hard-hearted and self-protective ^{13}C NMR spectroscopist. Many biological applications such as metabolic studies fall into this category. Samples are often measured in mouse-days, or other equally bizarre units. A mouse-day of some products might be from 10 to 50 micrograms.

Chart C: ¹³C spectrum

Sample: 3.5 mg. mixture of methyl esters of fatty acids.
Solvent: CDCl₃ (lock)
Acq. Time: 1.0 sec. Pulse delay: 5.0 sec.
No. Pulses: 8935 Time: ~15 hrs.

Olefinic carbon region.

Component	Label	NMR
18:3	3	3.2 %
18:2	50	47.2 %
18:1	35	35.2 %
18:0	12	14.4 %

C₉,₁₀ (18:1)
C₉,₁₃ (18:2)
C₁₀,₁₂ (18:2)
–O–CH₃
C₂ C₁₆
C₈,₁₁ (18:1), C₉,₁₄ (18:2); C₉ (18:0)
C₁₁,₁₄ (18:3)
C₃
C₁₁ (18:2)
C₁₇
C₁₈

Chart D: ¹³C spectrum

100 micrograms Cholesterol
Solvent: C₆D₆ (lock)
Acq. Time: 0.8 sec.
No. pulses: 300 K
Time: 66 ⅔ hrs.

With the idea of freeing the biochemist from the drudgery of mouse culture on a large scale, I decided to determine the lower limit of sample size which could give a usable ¹³C spectrum from a complex molecule with data accumulation over a weekend. Chart D shows the ¹³C spectrum of 100 micrograms of cholesterol dissolved in C₆D₆ and run for 300K transients at 0.8 sec. intervals. I believe that the capability demonstrated here should make ¹³C NMR applicable to some of these pitifully small samples resulting either from the physical size limitations of practical laboratory animals, or from the small scale of effective separation methods such as thin layer chromatography or GLC.

Sincerely,

James N. Shoolery

James N. Shoolery, Applications Chemist
NMR Applications Laboratory
Varian Associates
Palo Alto, California

The New *Products for NMR Brochure* from Aldrich

The new *Products for NMR* brochure contains many new products, new packaging schemes and improved isotopic purities. Aldrich has gained a well-deserved reputation in the deuterated solvents market by serving the needs of researchers and scientists worldwide for over 25 years. We have added quite a few new deuterated solvents packaged in screw-cap bottles to meet the ever-changing demands of our customers. Below is a list of these. For information on other deuterated solvents Aldrich has available, please refer to the *Products for NMR* brochure.

54,033-1	Acetone-d_6, 99.9 atom % D	10mL	$21.60
52,209-0	Acetone-d_6, 99.9 atom % D	10g	$24.20
	(*contains 0.03% v/v TMS*)		
52,214-7	Acetonitrile-d_3, 99.8 atom % D	10g	$33.10
52,210-4	Benzene-d_6, 99.6 atom % D	10g	$26.30
52,211-2	Dichloromethane-d_2, 99.8 atom % D	10g	$95.80
52,213-9	Methyl-d_3 alcohol-d, 99.8+ atom % D	10g	$62.40
52,212-0	(Methyl sulfoxide)-d_6, 99.9 atom % D	10g	$18.70
52,215-5	Pyridine-d_5, 99 atom % D	10g	$69.00
54,035-8	Toluene-d_8, 99.5 atom % D	10mL	$58.30

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- Thin-wall glass with round bottoms
- Sandblasted marking spot for labeling samples

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NMR TUBE SELECTION GUIDE

Choose the NMR tube grade that most closely matches the frequency (in MHz) of the spectrometer.

Aldrich Grade	MHz	Applications	Cross Ref. No. (5mm tubes) Wilmad®	Kontes®
Disposable	30	Student labs, basic studies	WG-Economy	–
Series 30	30	Student labs, basic studies	505-PS	897200
Series 200	60 to 270	Lower-field studies	506-PP	897205
Series 300	60 to 360	Routine applications	507-PP	897220
Series 400	200 to 500	High-field, multiple-scan FT-NMR	528-PP	897235
Series 500	500+	Ultra-high resolution	535-PP	897240
Series 800	600 to 800	Highest resolution and performance	541-PP	897245

Grade	L (in.)	Wall Uniformity (in., TIR)*	Camber (in.)	Cat. No.	Pkg/5	20 Pkgs
3mm Microsample NMR tubes						
Series 300	7	0.0020	0.0010	**Z41,290-2**	$44.60	$712.00
	8	0.0020	0.0011	**Z41,291-0**	50.70	810.20
Series 400	7	0.0010	0.0005	**Z41,292-9**	69.50	1,111.40
	8	0.0010	0.0006	**Z41,293-7**	78.80	1,259.80
Series 500	7	0.0005	0.00025	**Z41,294-5**	113.10	1,808.60
	8	0.0005	0.00035	**Z41,295-3**	127.80	2,137.60
5mm NMR tubes						
Disposable	7	–	–	**Z41,277-5**	12.90	–
Series 30	7	0.0030	0.002	**Z41,278-3**	28.70	457.00
Series 200	7	0.0025	0.002	**Z41,279-1**	31.40	501.80
Series 300	7	0.0020	0.0010	**Z41,280-5**	40.50	646.20
	8	0.0020	0.0011	**Z41,281-3**	45.40	725.60
	9	0.0020	0.0012	**Z41,282-1**	50.70	810.20
Series 400	7	0.0010	0.0005	**Z41,284-8**	61.20	977.60
	8	0.0010	0.0006	**Z41,285-6**	67.20	1,074.80
Series 500	7	0.0005	0.00025	**Z41,286-4**	86.90	1,389.40
	8	0.0005	0.00035	**Z41,287-2**	97.20	1,553.60
Series 800	7	0.0002	0.00015	**Z41,288-0**	202.25	3,236.50
	8	0.0002	0.00015	**Z41,289-9**	226.75	3,626.20
10mm NMR tubes						
Series 200	7	0.0030	0.0015	**Z41,296-1**	20.50/ea	391.25/25
Series 400	7	0.0015	0.0005	**Z41,298-8**	28.30/ea	540.00/25

* TIR-Total Indicator Reading

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June 15, 2001

(received 6/15/2001)

Professor B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

When a paperclip rings

Dear Barry,

Interference from resonant acoustic ringing (magnetostriction) of certain metals at the irradiation frequency is a major source of false alarms in the detection of explosives and contraband narcotics by ^{14}N nuclear quadrupole resonance[1] (NQR). Here NQR means no static magnetic field is applied. Our group has been looking for ways to eliminate the signal from acoustic ringing while keeping the NQR signal. To that end we have explored the use of three-frequency NQR, in which the sample containing ^{14}N ($I = 1$) is irradiated at two of its three characteristic NQR frequencies (ω_1, ω_2) and the signal is detected at the third NQR frequency ($\omega_3 = \omega_1 + \omega_2$). We found that under the correct conditions, the three-frequency signal can have a magnitude comparable to the more traditional single-frequency experiment[2]. Since no radio frequency (RF) energy is applied at the frequency of the receiver, interference from acoustic ringing and receiver dead time could be drastically reduced.

The oscillating magnetic field of the RF pulse produces small changes in the physical dimensions of ferromagnetic materials (magnetostrictive effect) and conversely, these physical deformations produce changes of magnetization in the material which can then be detected as an artifactual signal. The dashed line of Fig.1 shows the resulting response from a magnetized paper clip to a single-frequency pulse at $\omega_3/2\pi = 4.64$ MHz. For comparison, the response of an 8 g sample of sodium nitrite $NaNO_2$ to the same pulse is shown as a solid line. Following the same peak in frequency space (the starred one in Fig.1 (b)) we observed that the response of the paper clip to the RF pulse is linear both in the RF field strength and in the duration of the pulse. See the insets of Fig. 1 (b).

For *simultaneous* irradiation of the paperclip with the two frequencies ω_1 and ω_2 (3.60 MHz and 1.04 MHz) we observed a surprisingly strong acoustic ringing signal at ω_3 as shown by the dotted line of Fig. 2. However, for *serial* irradiation of the same paperclip first with ω_1 then with ω_2 **no** acoustic ringing at ω_3 was observed as shown in Fig. 3. The pulse parameters used in Fig. 2 and 3 are close to the optimum needed for an NQR signal for each sequence (the NQR signals are shown as solid lines). The fact that the acoustic ringing at ω_3 appears for simultaneous, not for serial irradiation, implies that the deformation of the paperclip in response to the oscillating magnetic field contains a large nonlinear component. We observed that paperclip's response was linear in the duration of the simultaneous pulse (not shown) and in the two field strengths B_1 and B_2 (shown in the insets of Fig. 2(b)). This suggests that the nonlinear component is proportional to the square of the total magnetic field.

Therefore the use of serial irradiation of the sample with ω_1 and ω_2 and detection at ω_3 looks like a promising means to detect a ^{14}N NQR signal, without interference from acoustic ringing. Furthermore, as can be seen in Fig. 1(a) and Fig. 3 (a), the receiver dead time is significantly reduced over that of a single-frequency experiment.
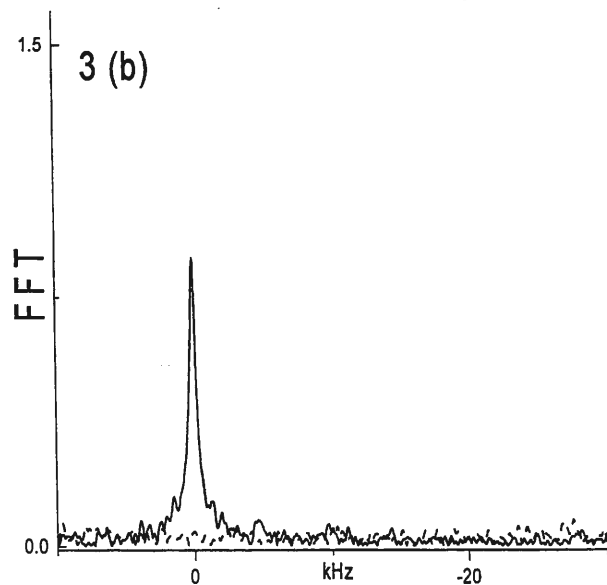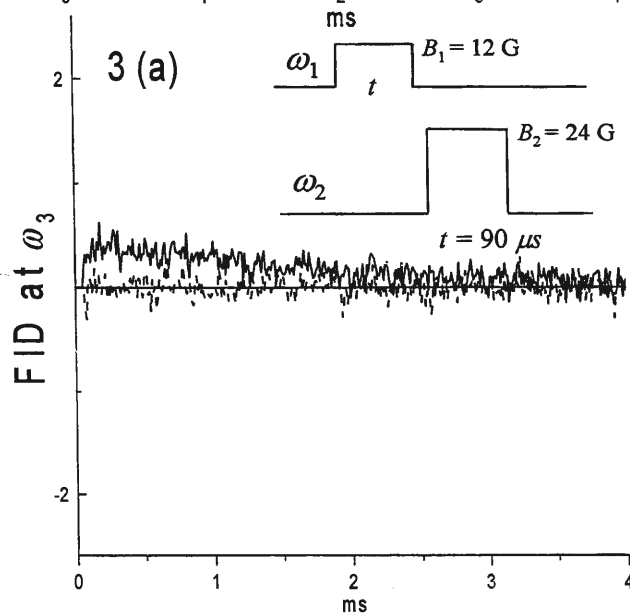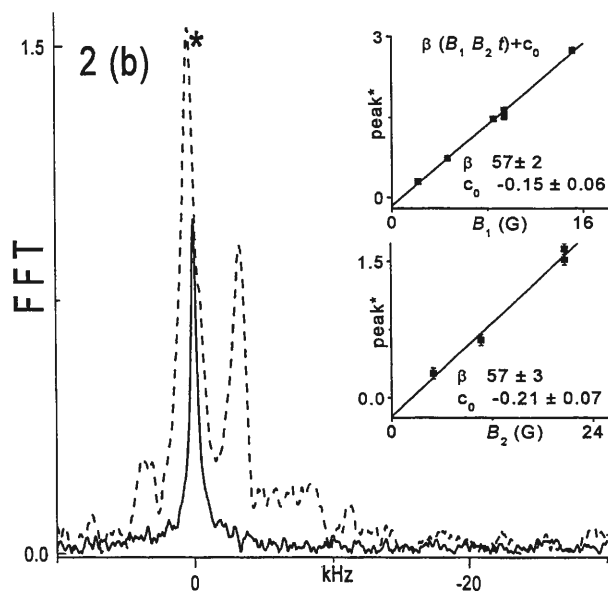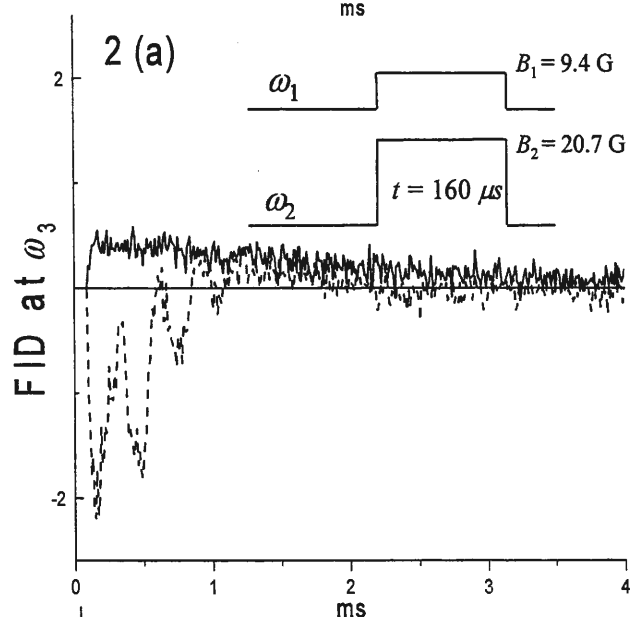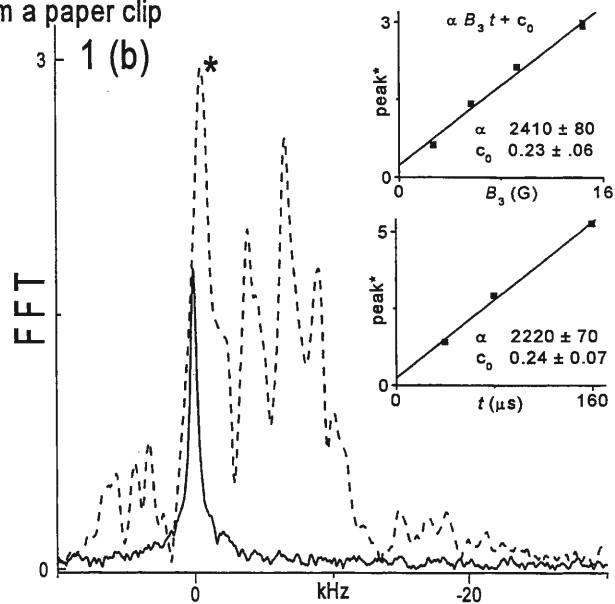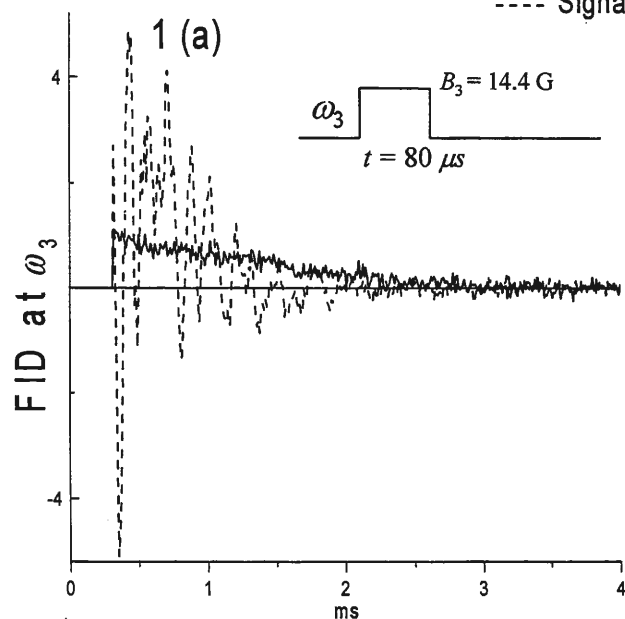
With best regards,

Karen Sauer

Karen L. Sauer

[1] A.N. Garroway, M.L. Buess, J.P. Yesinowski, J.B. Miller, R. A. Krauss, *Cargo Inspection Technologies - S.P.I.E. Proceedings Series* **2276** (1994) 139.
[2] K.L. Sauer, B. H. Suits, A.N. Garroway, J.B. Miller, to appear in *Chem. Phys. Lett.* 2001.

--- NQR signal from NaNO$_2$
- - - Signal from a paper clip

1 (a)

ω_3

$B_3 = 14.4$ G

$t = 80$ μs

FID at ω_3

1 (b)

FFT

$\alpha B_3 t + c_0$

α 2410 ± 80
c_0 0.23 ± .06

α 2220 ± 70
c_0 0.24 ± 0.07

t (μs)

2 (a)

ω_1 $B_1 = 9.4$ G

ω_2 $B_2 = 20.7$ G

$t = 160$ μs

FID at ω_3

2 (b)

FFT

$\beta (B_1 B_2 t) + c_0$

β 57 ± 2
c_0 -0.15 ± 0.06

B_1 (G)

β 57 ± 3
c_0 -0.21 ± 0.07

B_2 (G)

3 (a)

ω_1 $B_1 = 12$ G
t

ω_2 $B_2 = 24$ G

$t = 90$ μs

FID at ω_3

3 (b)

FFT

KUNGL TEKNISKA HÖGSKOLAN

VETENSKAP OCH KONST

Department of Chemistry, Physical Chemistry
Professor Peter Stilbs

Stockholm June 19, 2001

Page 1 of 2

(received 6/19/2001)

Professor B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto
CA 94303-3410
USA

Re: Integrals or peak heights ?

Dear Barry,

Thank you for your yellow Ultimatum.

When evaluating data from e.g. spin relaxation measurements or FT-PGSE NMR self-diffusion measurements one has the option to quantify intensities in terms of peak amplitudes or peak integrals. Many people seem to have a pre-conceived idea that integrals result from some kind of averaging process, and hence are S/N-enhancing, as compared to peak heights. This is wrong.

The integrated quantity is a changing function, and the integration limits are normally several bandwidths wide. The outer areas essentially contain no signal and just noise. They are also likely to have contributions from adjacent bandshapes. Integration also integrates any baseline problems, perhaps arising from slight phase instabilities of e.g. a dominant water signal in the spectra.

For a long time I have been convinced that the use of integrals is worse than use of peak heights in the typical case of FT-PGSE (or spin relaxation) data. One should avoid peak drift picking routines in spectrometer software in the case of noisy data, however. Otherwise, the signal gets an inappropriate bias to positive values when decayed to the level of noise in the spectra.

The following Figure illustrates 'Monte-Carlo simulations' of the effect of 'baseline noise' and 'intensity noise' on the error limits of the estimation of the time constant of an exponentially decaying data set, like in PGSE diffusion measurements. As seen, integrals

are no better than peak heights, and in the case of any baseline problem they are much worse, since the error gets integrated. A fuller report will ge given elsewhere.
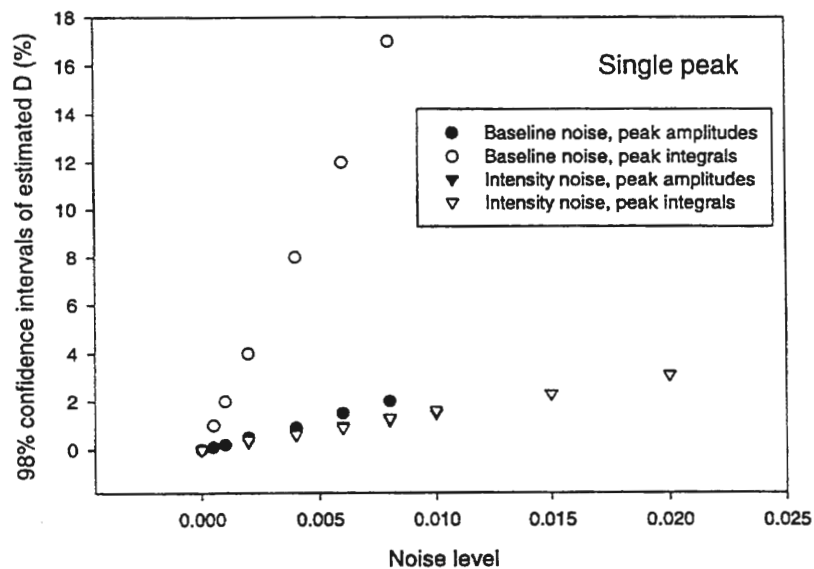
Yours Sincerely

Peter Stilbs

The NMR Newsletter - Book Reviews

Book Review Editor: István Pelczer, Dept. of Chemistry, Princeton University, Princeton, NJ 08544

Annual Reports on NMR Spectroscopy
Volume 41

Edited by

G. A. Webb

Academic Press Inc. (A Harcourt Science and Technology Company), London 2000, pp x + 322, ISBN 0-12-505341-X (Hardback) £84.95, $134.95

This volume in the well-established series consists of four reports on a variety of topics:

Cobalt-59 NMR Spectroscopy by Jerry C.C. Chan and Steve C. F. Au-Yeung; (54 pages, 204 references). This is the first review in the series devoted entirely to cobalt spectroscopy, which was covered in more general articles in 1979-80. Cobalt was one of the elements studied in the early work on nmr, and is still under exploited. While its receptivity is good (1570 times that of ^{13}C), the quadrupole associated with the 7/2 spin means that its study is not routine. This review devotes most space to solid state studies and in particular single-crystal nmr. Other major sections cover solution-state nmr and theoretical studies (calculations of chemical shielding tensors and quadrupole coupling constants).

Advances in Theoretical and Physical Aspects of Spin-Spin Coupling Constants by Rubén H. Contreras, Juan E. Peralta, Claudia G. Giribet, Martin C. Ruiz de Azúa, and Julio C. Facelli. This is the longest review in the book (130 pages, 710 references) and follows on from an earlier review in volume 27 (1993) by two of the present authors. The major headings are calculations on quantum exchange couplings and couplings originating in electron-nucleus interactions, intra- and inter-molecular interaction effects on spin-spin coupling constants.

Dipolar Recoupling [sic] under Magic-Angle Spinning Calculations by Stephan Dusold and Angelika Sebald. This article (80 pages, 198 references) reviews a technique which, although based on principles known for some time, has come to the fore recently. Its importance lies in the fact that high resolution solid state nmr provides (by using dipolar coupling constants) a means of abstracting inter atomic distance information. Under magic angle spinning conditions this information is usually lost; this article discusses methods of regaining it.

Characterization of Porous Media Using NMR Methods by Patrick J. Barrie. (52 pages, 198 references) This article is the one in the book that deals with *applications* of solid state nmr. The author makes the point that nmr affords a non-invasive and non-destructive means of looking at the pore structure of solids, which is applicable in areas as diverse as soil sciences, food processing, separation techniques, and polymer science. The results most usually take the form of parameters abstracted from spectra, but the review also discusses methods of producing images of (for example) the spaces between glass beads immersed in flowing water. This latter technique allows the measurement of flow velocities.

This review series has a long history. It has been expertly edited for most of the time by Graham Webb. It is worth mentioning that volumes 39 and 40 provide cumulative indices to the first 38 volumes, though it is hard to see why these indices (totalling 542 pages) needed to be split into two volumes. The breadth of the coverage in the series, as a whole, demands it should be in the library of any organisation involved in nmr.

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June 21, 2001

Dr. Barry L. Shapiro,
The NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303
USA

(received 6/21/2001)

Dear Barry:

SUBJECT: CONTRACT RESEARCH OPPORTUNITY

We are a fairly well equipped industrial NMR group and as a pilot study within our Company we are being encouraged to spend a small amount of our time providing a contract research service to non-Unilever customers. This could be anything from simply providing access to some our NMR facilities through to applying our research expertise to help solve complex problems.

Our NMR facilities are as follows:

1) **Bruker DSX300 NMR spectrometer**

- CPMAS (range $^2H - {}^{31}P$)

- HRMAS inverse probe with gradient coils

- Z – diffusion (^1H with gradient strength ~10T/m)

- Microimaging (^1H, ^2H and ^{23}Na)

2) **Bruker AMX400 NMR spectrometer**

- 5 mm dual $^1H/^{13}C$

- 5mm BB inverse with z gradient (strength ~1.6T/m)

- 10 mm VSP probe

- LCNMR capability

All with VT capability on both instruments

3) **Resonance Instruments MARAN 10 MHz NMR spectrometer**

- 40mm ^1H ambient temperature probehead

- 18mm ^1H VT probehead with triple gradients.

  This instrument is used for:

    - relaxation time measurements
    - diffusion coefficient measurements

June 21, 2001

- 1D profiling measurements

- MRI measurements

- NMR MOUSE experiments

4) **Resonance Instruments MARAN 20 MHz NMR spectrometer**

- 18mm ^{1}H VT probehead with double gradients
- 10mm ^{1}H VT probehead with double gradients
- 18mm ^{2}H VT probehead with double gradients

This instrument is used for:

- routine solid/liquid measurements

- droplet sizing

- relaxation time measurements

- diffusion coefficient measurements

-   1D profiling measurements

Anyone interested in exploring the opportunity of using any our capabilities is encouraged to contact us either at the above address or directly via e-mail.

With kind regards

Steve Ablett   Adrienne Davis   Dave Martin
(steve.ablett@unilever.com)   (adrienne.davis@unilever.com)   (dave.r.martin@unilever.com)
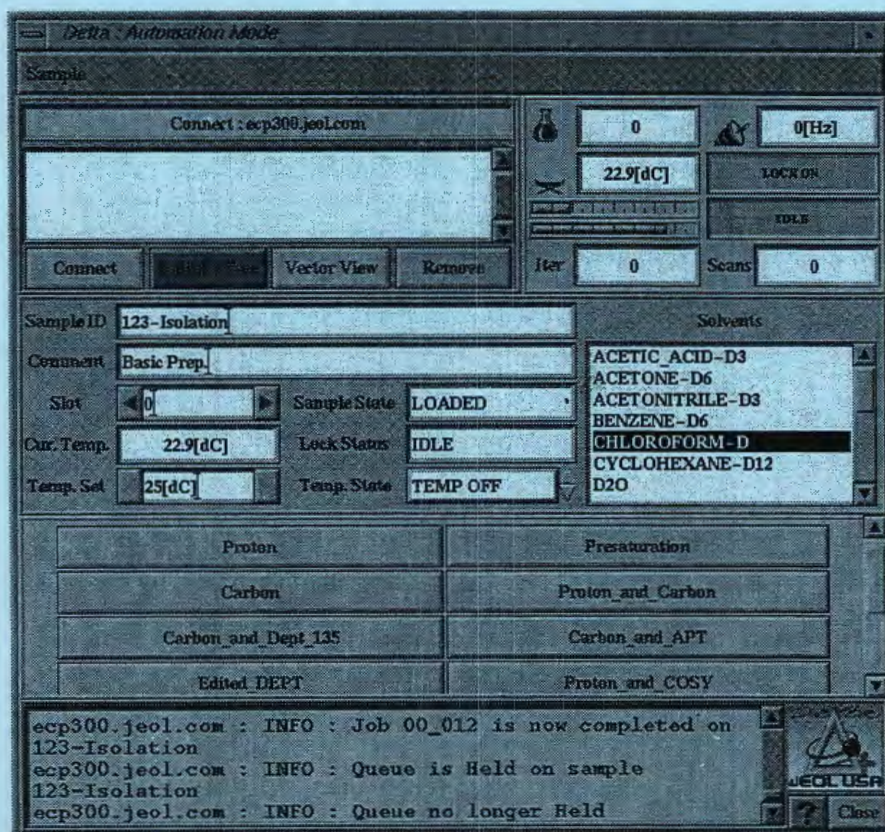
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