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\[ a) 21{}^\circ C \]

\[ b) -95{}^\circ C \]

\[ c) -138{}^\circ C \]

13C (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) 1H-13C cross polarization. b) Bloch decay. The peak at ~90ppm is due to the Delrin rotor.

JEOL

235 Birchwood Ave, Cranford, NJ 07016
(201) 272-8920
June 30, 1983

Professor B. L. Shapiro
Texas A & M NMR Newsletter
College Station, Texas 77843
U.S.A.

Dear Barry:

1) NO₃ rotations in solid NH₄NO₃

Ammonium nitrate is known to undergo at least five different solid-solid phase transitions. There has been considerable debate in the literature about the rotational motion of the nitrate ion in the high temperature phase (1). We have carried out a few simple nitrogen nmr experiments which are most useful in characterizing the behaviour of the nitrate ion. Proton-decoupled nitrogen-15 nmr spectra of the solid I (T = 403 K) and solid II (T = 373 K) phases of NH₄NO₃ are shown in fig. 1. The ¹⁵NO₃ and ¹⁵NH₄ resonances have opposite phases but for easier presentation are both plotted with identical phases. The spectra indicate that in the solid I phase rotations of the nitrate ion are rapid with respect to the ¹⁵N chemical shielding anisotropy. A more quantitative measure of the effect correlation time for nitrate ion rotations can be obtained by measuring ¹⁴N T₁'s. E.g., at 413 K, T₁ (¹⁴N) = 14.6 ms which implies τₑff = 8 ps.

2) Unusual Coupling

In a recent letter (294-25) one of your readers suggested ¹⁴J(OH₄H₆) = 6 Hz in I. If correct I would agree that this is a most unusual coupling being at least an order of magnitude greater than would be expected. I would suggest that the assignment of H₄ and H₆ should be reversed and the 6 Hz coupling be attributed to ³J(NH, H₆)².

Best wishes from Nova Scotia.

Yours sincerely,

[Signature]

Roderick E. Wasylishen
Associate Professor

REW/djc

$373\, K$

$403\, K$

NO$_3^-$  \hspace{1cm}  NH$_4^+$
July 8, 1983

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

Dear Prof. Shapiro:

Yet another simple Test for \(^{13}C\)-Multiplicity on a VARIAN XL-100

There exist now some new experiments to determine carbon multiplicities. In contrast to the well known off-resonance technique they show almost equal sensitivity compared to the normal broadband decoupled carbon spectra and don't suffer from overlap of multiplet lines in spectra with a high density of signals. Multiplet selection in these new procedures is based on relative phase and intensity of proton broadband decoupled carbon signals, which are different for C, CH, CH\(_2\) and CH\(_3\).

The attempt to adapt some of the modern pulseschemes on an older type spectrometer fails mainly due to the fact, that these machines are not equipped with a RF-90°-phase-shifter. Long 90°-pulselengths - if not equipped with a pulseamplifier - and single phase detection mode on the other hand don't guarantee uniform flip angles over the entire frequency range. This leads to poor sensitivity for some lines, phasing problems and thus ambiguities in multiplicity determination. We referred therefore to the simple one-pulse method with delayed decoupling as proposed by Le Coq et al. some time ago [1].

In contrast to this original version which leads to severe phasing problems and line shape distortions caused by the delayed sampling, we start the detection of the FID immediately after the pulse as visualized in Fig. 1. The first part of the FID which contains the carbon signal under proton coupled conditions hardly contributes to the spectrum, which shows only the signals determined under proton decoupling in the second part. Simplicity both in setting up the experiment and modifying the hardware, no problems with phasing and the determination of 90° pulselengths - we use pulselengths optimized for maximum sensitivity - are the main advantages of this variant. Some slight loss of sensitivity for proton bearing carbons, compared to a normal broadband decoupled spectrum and some baseline roll are the disadvantages.

Fig. 2 shows two spectra of Isocadron with delays optimized to show all carbon signals with appreciable sensitivity a) and set to suppress signals with \(^1J\) \(_{CH} > \)125 Hz b). Spectrum a) shows CH and CH\(_3\) with negative, C and CH\(_2\) with positive intensities. (Continued on p. 6)
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From spectrum b) one immediately recognizes five signals with relative high intensities, the quaternary (positive), the two olefinic and the two cyclopropane methine carbons.


Sincerely yours

Peter Bigler

---

**Fig. 1**

**Fig. 2**
6th July, 1983

Dear Barry,

T1 Values for $^{17}$O in Metallocarbonyls

About five or six years ago we started to look at $^{17}$O spectra of some small heterocycles supplied by Rosanna Mondelli from Milan to supplement the $^{13}$C and $^{15}$N data we had. We used our now defunct Brucker HFX-13 (vintage 1970) and obtained the normal, quite broad, spectra which one had come to expect. One of our other Italian collaborations was with the inorganic chemists at the University of Turin. This had led to our early $^{13}$C work on metallocarbonyls and the collaboration was still occasionally activated. Because of this Silvio Aime visited us about 1978 and suggested we should try $^{17}$O work on metallocarbonyls - something that had not occurred to us as being useful since we were conditioned to expecting broad lines. We concurred and obtained delightful $^{17}$O spectra with narrow lines. This opened up the possibility of high resolution $^{17}$O work on metallocarbonyls such as the study we then did on Co$_4$(CO)$_{12}$, for which $^{13}$C work had been enigmatic. By this time we had access to the London University Bruker WH-400.

The latest news is that we have been measuring T1 values for $^{17}$O in metallocarbonyls. Normally the samples are prepared in Turin, enriched in $^{17}$O and arrive in London by a variety of means - normally in someone's holiday baggage.

For Fe(CO)$_5$ (measured at natural abundance) we found the $^{17}$O T1 value (toluene solution; 298 K) to be 50 ms. Use of the Stokes-Debye formula gave $\tau_C$ as 4.6 ps which compares well with the literature value$^3$ for the T1 range in the temperature interval 253-313 K (pure liquid) of 3.5-9.0 ps. The derived value for the $^{17}$O quadrupole coupling constant (QCC) is 2.13 MHz. This is smaller than the value for free CO (4.34 MHz)$^4$. For other metallocarbonyls we have found T1 to be in the range 50-8 ms so far, and we have calculated the QCC range to be 2.0-3.3 MHz. Interestingly T1 varies from one CO to another within the same compound. For example, in Re$_2$(CO)$_6$ we find 29.4 ms for the axial CO s and 13.2 ms for the equatorial CO s. The difference is in the wrong sense for preferred rotation around the Re-Re bond and we deduce that QCC values are structure related. The work has been accepted for publication in Chemical Communication$^5$ if readers want details.
Other work here has included some saturation transfer experiments which Geoff Hawkes inspired (and did!) to study slow carbonyl exchange in $H_2Os_3(CO)_{10}$ ($^{13}C$ enriched). This led to some elegant 2D-spectra on the same sample to pick up not only the exchange but also the $^{13}C$-$^{13}C$ coupling.

Not content with all this, Silvio Aime and his colleagues have been producing $^2H$ enriched hydrido metallocarbonyls and we accordingly have a programme of $^2H$ work. Until it comes to fruition and your next reminder arrives,

Best wishes from the Group,

Yours sincerely,

Professor E.W. Randall

Dear Barry,

Condensation of sodium counterions around micelles: experiment and theory.

We had applied successfully earlier a modified Poisson-Boltzmann treatment to systems, synthetic or natural, constituted of cylindrical polyelectrolyte molecules in an ionic atmosphere\textsuperscript{1-2}. We have now extended this formalism to micellar aggregates: the concept of counterion condensation, as borrowed from the definition by Westra and Leyte\textsuperscript{3}, is generalized for this purpose to polyelectrolytes of spherical symmetry. The calculated ionic activities agree very well with experimental activities from the literature.

As yet another test of the model, sodium-23 nmr linewidths are measured for sodium dodecyl sulfate, in the range of ca. 10\textsuperscript{-1} cmc - 10 cmc. They show outstanding agreement with the mean value of the calculated \((\text{efg})^2 = \langle V/r \rangle^2\): the line broadenings are directly proportional to \(\langle V/r \rangle^2\). From the slope, taken together with a mean viscosity of 9 mP (the entire viscosity range extends from 8.5 to 10.8 mP), we obtain a value of 41 ns for the product \((1 + \gamma_0)^2 \tau_c\). Our experimental results are also consistent with the notion of a pre-aggregation, prior to micelle formation, at concentrations below the cmc. Hence, we are confident that the modified Poisson-Boltzmann approach will prove more generally useful in studying micelles.

Otherwise, we are eagerly awaiting delivery at the end of the summer of a new Bruker 300 wide bore spectrometer for our group. Micelles are not the only organized bodies of interest to us. We are also busy investigating ionic...
transport across membranes, in relation with the metabolism, both normal and pathological. So that the new instrument will come in handy for these other and more biological studies.

Did you know that Belgium has now three three-stars restaurants in the Michelin Guide? Which makes your visit here even more overdue!

With best personal regards,

Cordially yours,

A. Delville

P. Laszlo

References:

July 12, 1983

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

Dear Professor Shapiro:

CURVE DECONVOLUTION OF ESR SPECTRA ON THE NMR COMPUTER

Our laboratory has two Nicolet-360 WB NMR spectrometers and one Nicolet data station, interfaced to an IBM ER200-D-SRC electron spin resonance spectrometer and (recently) to a Varian EM390 proton spectrometer. All three instruments are based on the Nicolet 1280 computer with CDC-9427H disk drives.

The general signal averaging computer program supplied by Nicolet Instrument Corp. (Madison, Wisconsin) for the ESR data station is called LAB2. This versatile program can accept just about any analog signal as input and then perform a multitude of data handling routines, e.g. Fourier transformation, spectral addition, integration, phase correction, and plotting of spectra. However, there is no provision in the LAB2 program to do curve deconvolution.

The NMC program supplied by Nicolet Magnetics Corp. (Fremont, California) to operate their NMR equipment is capable of doing curve deconvolution. Unfortunately the NMR program will not recognize disk files generated by the LAB2 program. The NMC program recalls a file from the disk by searching for the file name, verifying that the file header is under NMC header, and then loading the file into computer memory. In order to force LAB2 data files into the NMC program, there are a few things that need to be known: (1) our computers contain 128K RAM; (2) the NMC program occupies the first 64K of memory; (3) the data memory is the second 64K of RAM; and (4) the files are stored on disk with the file header at the beginning of the file. Hence if the file can be loaded into the data memory area (second 64K) before the NMC program is loaded, the data should be available for the NMC program. The following diagram will be used to explain how this can be accomplished:
The file is loaded from monitor into computer memory such that the file header is in the first 64K and the data is in the second 64K. When the NMC program is loaded, the header is overwritten by the NMC program, but the data remains intact. The following commands are used:

With the computer in monitor.

* LOAD FILE NAME 177240 <ret>
* RUN NMC <ret>
> CB select the correct block size for your data

Your data will be in block No. 0. If you wish to save the data on disk, use the appropriate NMC command which will create a disk file with an NMC header. Data stored in this manner can be recalled from the NMC program and treated as NMC data. All data handling routines available in NMC may be used, e.g. curve deconvolution, line fitting, IC base line straightening, integration, plotting, expansion, etc.

Please credit this contribution to the Hercules Research Center account. I wish to thank Dr. D. L. Dalrymple of NMC for assistance in this work.

Yours very truly,

David A. Smith
Analytical Division

DAS:bjm
About approaches used for interpreting carbon-13 relaxation data in systems involving a fast motion superimposed on a slow motion

Dear Professor Shapiro,

When carbon-13 longitudinal relaxation times of an alkyl chain are frequency dependent, although ranging at relatively high values (of the order of a second), and/or the nuclear Overhauser factor is less than its maximum value, this indicates the presence of a slower motion superimposed on a fast motion due to internal rotations. This situation is encountered in side-chains of polymers or peptides as well as in surfactants engaged in micelles or lyotropic mesophases. Some procedures available for interpreting such relaxation data make use of two correlation times (\(\tau_R\) and \(\tau_G\) for the slow and fast motions, respectively). Two of them lead to the same formulae: the "two-step model" originating from the Lund group (1) and the so-called "model free approach" of Lipari and Szabo (2):

\[
\frac{1}{T_1} = \frac{1}{T_1^{\text{local}}} \left( \frac{1}{T_1^{\text{general}}} \right) = \left( \frac{1}{T_1^{\text{model free}}} \right) = \left( \frac{1}{T_1^{\text{Woessner}}} \right)
\]

\[
\frac{1}{T_1} = \frac{1}{T_1^{\text{local}}} \left( \frac{1}{T_1^{\text{general}}} \right) = \left( \frac{1}{T_1^{\text{model free}}} \right) = \left( \frac{1}{T_1^{\text{Woessner}}} \right)
\]

This formula applies for a carbon bonded to a single proton; all symbols have their usual meaning. \(S\) is a "local" (two-step model) or a "generalized" (model free approach) order parameter. Within the frame of the model free approach, \([1]\) is valid provided that \(\tau_G < \tau_R\) and that \((\omega\tau_G)^2 < 1\) for any considered \(\omega\). If one applies these latter conditions to the well-known Woessner's formula \([3]\), one obtains:

\[
\frac{1}{T_1} = \frac{1}{T_1^{\text{Woessner}}} = \left( \frac{1}{T_1^{\text{Woessner}}} \right)
\]

As a matter of fact, this model can also be used \([4]\) to interpret carbon relaxation data of alkyl chains whose one extremity is attached to a slowly reorienting body (in micelles, for instance). In that case, \(\theta\) must be considered as the angle between the CH bond and a virtual axis around which the CH vector is assumed to rotate. (This virtual axis is defined according to the cumulative effect of rotations around all C-C bonds). Regarding the slow motion contribution, formulae \([1]\) and \([2]\) are seen to be formally identical provided that \(\frac{1}{4}(3\cos^2\theta - 1)\) is identified as \(S^2\). The
coefficient in front of \( \gamma_C \) in \([2]\) never differs by more than 15% from \( [1-\frac{1}{3}(3\cos^2\theta-1)]^2 \). Therefore, the interpreting procedures represented by formulae \([1]\) and \([2]\) appear to be very similar.

Finally, it should be mentioned that exponential correlation functions have been assumed throughout. This is far from being warranted for the slow motion especially in micelles or lyotropic mesophases. This problem can be circumvented in the following way. If measurements have been performed at different frequencies, \( \gamma_g \) can be fitted at each frequency using \([1]\) or \([2]\) and its numerical value reinserted in

\[
\left[ \frac{3\gamma_R}{1+\omega^2/\omega_c^2} + \frac{\gamma_R}{1+(\omega_H-\omega_c)^2/\omega_c^2} + \frac{6\gamma_R}{1+(\omega_H+\omega_c)^2/\omega_c^2} \right]
\]

This yields numerical values (as a function of the frequency) for what would be the spectral density pertaining to the slow motion. Although this procedure is rather approximate (three different \( \omega \) are involved), it should provide some insight into the frequency dependence of these spectral densities.

Yours sincerely,

\[\text{CANET}\]

---

(1) H. Wennerström, B. Lindman, O. Söderman, T. Drakenberg and J.B. Rosenholm
T. Ahlnäs, O. Söderman, C. Hjelm and B. Lindman

(2) G. Lipari and A. Szabo
ibid. 104, 4559 (1982)

(3) D.E. Wossner

(4) D. Canet, J. Brondeau, H. Nery and J.P. Marchal
Chem. Phys. Lett. 72, 184, (1980)
D. Canet, J.P. Marchal, H. Nery, B. Robin-Lherbier and J.M. Cases
J. Colloid Interf. Sci., 93, 241 (1983)
Identification of Polyamines in Plant Viruses by $^1$H NMR.

A number of plant viruses and bacteriophages are known to have different amounts of polyamines. Identification and quantitation of these molecules involve detailed chemical procedures in combination with GC/MS methods. We report here a simple and nondestructive way of identifying polyamines in plant viruses by $^1$H NMR.

The figure shows high-field $^1$H NMR spectra at 470 MHz of (a) turnip yellow mosaic virus (TYMV) and (b) spermidine-treated and (c) native belladonna mottle virus (BDMV). The three broad peaks in spectrum (a) are assigned to polyamines based on their chemical shift similarity to those of free spermine/spermidine and from the chemical information that TYMV contains about 400 polyamine molecules (predominantly spermidine) per virion. It is apparent from spectrum (c) that native BDMV does not contain any polyamine although it belongs to the same family as TYMV. However, spermidine is able to penetrate the protein shell of BDMV and irreversibly bind to the RNA as revealed by spectrum (b) which was obtained from spermidine-treated BDMV. We found from $^{31}$P NMR and analytical ultracentrifugation studies that native BDMV is unstable above neutral pH whereas TYMV is known to be stable up to pH 11.5. We attribute the instability of BDMV to the lack of polyamine in the virus particle. Spermidine-treated BDMV not only gives rise to a spectrum similar to that of TYMV but is also stable at high pH (11.5).
We hope to utilize these small molecule inclusions as NMR probes to study the behavior of a large system like a virus particle (mol. wt. -7 million). These results are described in a paper to appear in *Virology*.

Yours sincerely,

J.L. Markley  
R. Virudachalam

---

**Figure.** $^1$H NMR spectra (high-field region) at 470 MHz of (a) turnip yellow mosaic virus, (b) spermidine-treated, and (c) native belladonna mottle virus.
July 6, 1983

Professor Bernard L. Shapiro
Editor and Publisher
TAMU NMR Newsletter
Texas A & M University
Department of Chemistry
College Station, TX 77843

Dear Barry:

OPTIMIZATION OF S/N FOR SURFACE COIL NMR

One never seems to have enough S/N when applying NMR to biological systems. Sensitivity problems can be especially acute in the case of intact tissue samples where one confronts not only low concentrations but also lossy conducting samples and often less-than-optimal r.f. antennae. A particular case of interest to us has been the use of surface coil antennae to monitor ongoing in vivo biochemistry.

To develop techniques for maximization of S/N we let the Washington University IBM-370 consider the case of an ideal single-turn, flat, circular surface coil operating in the single-coil mode and placed against a large homogeneous sample. The results, shown in the accompanying figure, are reminiscent of those in elegant paper by Becker, Ferretti and Gambhir [Anal. Chem., 51, 1413-1420 (1979)]. As with the homogeneous B\textsubscript{1} of conventional coils, a significant increase in S/N may be obtained with surface coils by optimizing pulse repetition rate and pulse width. In practice this is straightforward to do empirically by setting the interpulse spacing $T_{\text{Acquisition Time}} \approx 2-3T_{1}^{*}$ and then experimentally determining the pulse width that provides maximum S/N.

Sincerely,

[Signatures]

Figure Caption

A plot of theoretical and experimental maximum integrated S/N per unit time as a function of pulse repetition period, $T/T_{1}$. The curves are the theoretical results for the sample starting 0.10 radii (solid line) and 0.15 radii (broken line) from the plane of the surface coil. The symbols represent experimental data at two different frequencies (30 MHz for H-2 and 188 MHz for F-19) for a large homogeneous sample starting 0.10-0.15 radii from the plane of the surface coil.

(Continued on p. 20)
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Bernard L. Shapiro  
Editor and Publisher  
TAMU NMR Newsletter  
Texas A&M University  
Department of Chemistry  
College Station, TX 77843

July 15, 1983

Dear Professor Shapiro:

The Blue Hen NMR Complex continues on its merry way. Lila, Joe, and Roger continue investigation of interesting problems with solution-state NMR spectroscopy, while I only scratch the surface of problems in catalytic chemistry. Most recently, we have held our 4th Delaware NMR Symposium on June 8. It was a tremendous success. If anyone would like to be included on future mailings, please contact Lila Giersch, Joe Noggle, Roger Crecely, or me and we shall make an effort to notify you of the 5th.

Other recent developments include the installation of our new AM-250 Bruker NMR spectrometer with its Aspect 3000 computer which, in addition to the WM-250, gives us the capacity we have needed for some time.

A small tidbit of the things you can do at surfaces. Supported metals are often used for hydrogenations and dehydrogenations. Attached are some spectra hot off the spectrometer of what you see when you combine benzene with a supported metal catalyst which has previously been treated with hydrogen and outgassed. You see cyclohexane! We have been able to monitor kinetics of this reaction with proton NMR in some very recent experiments over this catalyst. Not all catalysts allow this discrimination, because the broadening of the resonances of these physically adsorbed species may be severe depending on the nature of the catalyst. Thus, NMR spectroscopy is potentially very useful for the study of catalysts.

This communication should be credited to Joe Noggle, whose regards I send with mine.

Yours truly,

Cecil R. Dybowski  
Associate Professor of Chemistry

Enclosure
REDUCED SAMPLE
+ C6H6

CALCINED SAMPLE
+ C6H6

CALCINED SAMPLE
+ C6H12

REDUCED SAMPLE
+ C6H12

REDUCED SAMPLE
+ XS C6H6
Professor Bernard L. Shapiro  
Texas A and M University  
College of Science  
Department of chemistry  
College Station, TX 77843  

Dear Barry,

We are continuing our studies of in vitro and in vivo enzyme catalyzed rates of reactions by 2D FTNMR. In our first study of the anomerization and isomerization of glucose-6-phosphate and fructose-6-phosphate, we were able to obtain the various reaction rates involved. As a bonus we were also able to deduce the rate limiting steps in the reaction.

We have expanded our studies to more complex enzyme systems and have been successful in quantitating our results for adenylyl kinase, creatine phosphokinase, and the carbonic anhydrase reaction. Most recently we have measured the in vivo unidirectional flux between creatine phosphate (CrP) and adenosine triphosphate (ATP) in the leg and head of an anesthetized rat in a specially constructed probe with an animal cradle.

CrP + ADP + E ➔ CrP|ADP ➔ CREATP ➔ Cr + ATP + E

These studies are being carried out in collaboration with Drs. Howard Kantor and Robert Balaban, also of the National Heart, Lung and Blood Institute.

In Figure 1 is the 2D contour plot of the data obtained from the rat leg with a mixing time of 600 msec. A single 2D spectrum can be obtained in a few hours. The volumes of the cross peaks are a direct measure of the exchange rates in the initial velocity approximation. The experiment is repeated various times using different mixing periods to obtain the time dependance of the cross peak volumes. These results are shown in figure 2 for the rat leg. The unidirectional flux for CrP going to ATP was 13 umoles/g/sec in the leg and 2 umoles/g/sec in the head. Please credit this to the subscription of Bob Highet, the chagrined recipient of the notorious yellow reminder.

Sincerely,

James A. Ferretti  
Laboratory of Chemistry  
National Heart, Lung and Blood Institute
FIGURE 1.

FIGURE 2.
July 22, 1983.

17O Chemical Shifts of Substituted Uridines.

Dear Barry:

I want to take this opportunity, as my first contribution to the newsletter, to present some interesting 17O NMR data obtained while working in the laboratory of Dr. Steven Danylik at Argonne National Laboratory. As part of a continuing study of 17O NMR of uridine nucleosides, we studied the effects of substitution in the uracil ring on the 17O shifts of the carbonyl oxygens in both protic (H2O) and aprotic (CH3CN) solvents. The samples used were synthesized by Dr. Malcolm MacCoss with ~50% 17O enrichment selectively in either the 02 or 04 oxygen. A table of limited results appears below. The data on a more extensive number of compounds is being prepared for publication in the future.

The data in CH3CN indicate firstly that substitution at the uracil 5 position causes significant effects at 04 but minimal perturbation at 02. This is understandable in terms of an 04-C4-C5-C6 conjugation which does not include 02. The differences in H-bonding to H2O indicated by the differences Δ are consistent with previous experimental and theoretical data indicating only one lone pair is available for H bonding to solvent at 02, but both are available on 04.

One final observation is the relative effects the substituents have on the conjugated π electron system as evidenced by the 04 shifts in CH3CN.

1. R = H 2',3'-O-ISOPROPYLIDENEURIDINE
2. R = CH3 2',3'-O-ISOPROPYLIDENEISOBOSYLTYRINE
3. R = F 2',3'-O-ISOPROPYLIDENE-5-FLOURUPACIL
4. 2',3'-O-ISOPROPYLIDENE-5,6-DIHYDROURIDINE
17O Chemical Shifts

<table>
<thead>
<tr>
<th>Labeled Compound</th>
<th>CH3CN</th>
<th>H2O</th>
<th>( \Delta^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4-17O] I</td>
<td>333 ± 2</td>
<td>294 ± 6</td>
<td>39</td>
</tr>
<tr>
<td>[4-17O] II</td>
<td>333 ± 2</td>
<td>288 ± 8</td>
<td>45</td>
</tr>
<tr>
<td>[4-17O] III</td>
<td>323 ± 3</td>
<td>288 ± 4</td>
<td>35</td>
</tr>
<tr>
<td>[4-17O] IV</td>
<td>374 ± 3</td>
<td>344 ± 3</td>
<td>30</td>
</tr>
<tr>
<td>[2-17O] I</td>
<td>259 ± 1</td>
<td>246 ± 4</td>
<td>13</td>
</tr>
<tr>
<td>[2-17O] II</td>
<td>250 ± 2</td>
<td>234 ± 7</td>
<td>16</td>
</tr>
<tr>
<td>[2-17O] III</td>
<td>255 ± 3</td>
<td>239 ± 3</td>
<td>16</td>
</tr>
<tr>
<td>[2-17O] IV</td>
<td>260 ± 2</td>
<td>246 ± 4</td>
<td>14</td>
</tr>
</tbody>
</table>

a. Chemical shifts are reported in ppm downfield from H2O (29°C).
b. \( \Delta = \delta_{\text{CH}_3\text{CN}} - \delta_{\text{H}_2\text{O}} \)

Best regards,

Dr. Herbert M. Schwartz
Director, Major Instrumentation Center

1. Current address; Domtar Inc., Senneville, Quebec, H9X 3L7, CANADA.
4. Current address; Merck Sharp and Dohme Research Laboratory, P.O. Box 2000, Rahway, NY 07065.
July 1, 1983

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

Title: Internal Motion of DNA in Hydrated Fibers

Dear Barry:

It is a little surprise to us that a rapid internal motion with a large amplitude occurs in DNA fibers at high relative humidity, just as observed for DNA in solution. Figure 1 shows the $^{31}$P solid-state NMR spectra (40.3 MHz) and the observed relaxation times of $T_1$ and $T_2$ of B-DNA fibers at 98% relative humidity, for which the fibers are oriented parallel and perpendicular and 45° relative to the magnetic field. Clearly, these relaxation times reveal anisotropic effects: the relaxation times for parallel orientation of DNA fibers is about twice shorter than those for the perpendicular.

We have shown that the interpretation for these anisotropic effects requires the following motional modes within a DNA: two-site jump as a simplified rapid internal motion, rotation about the helical axis and bending or wobbling motion of the DNA strands. For two-site jump the rate of $6 \times 10^7$ sec$^{-1}$ and the amplitude of ±40° were estimated, the diffusion rate of about $10^5$ sec$^{-1}$ for the rotational motion about the helical axis and the amplitude of about ±25° for the bending motion.

There are many NMR studies on the internal motion of DNA in solution and most of the results are consistent with each other in that a rapid internal motion has a correlation time of nanosec. Therefore, we can state that the dynamic behaviors of DNA in solution is very much similar to that of DNA in hydrated fibers.

\[ T_1 = 1.17 \text{ s} \quad T_1 = 2.10 \text{ s} \]
\[ T_2 = 1.78 \text{ ms} \quad T_2 = 2.61 \text{ ms} \]

\[ \text{PARALLEL} \quad \text{PERPENDICULAR} \quad 45^\circ \]

Fig. 1. Cross-polarized $^{31}$P spectra of DNA fibers at different orientations relative to $H_0$.


Sincerely Yours,

Heisaburo Shindo
Title: "Geminal Methylgroups"

Dear Dr. Shapiro,

Recently we analyzed the structure of a tricyclic derivative of barbituric acid (A).

Geminal methyl groups exhibit couplings which are less frequently encountered in the literature. The most intense cross peak in the COSY spectrum connects these methyl signals. From the J resolved spectrum, we take the constant $J_{HH} = 0.65$ Hz, not a negligible quantity in spectrum simulation. As a matter of fact it is exactly one third of the four bond W-coupling in a rigid molecular backbone (f.e. 1.5 - 2.0 Hz in steroids).

The carbon signals of these methyl groups are split by three bond coupling between the protons of the geminal CH$_3$ and 6a-H. The latter coupling amounts to 4 Hz with the upfield methyl carbon and 3 Hz with the downfield methyl carbon. Hence, if we assume a Karplus type dependence of $J_{CH}$, we have criteria for the axial vs equatorial assignment.

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

Dear Professor Shapiro,

"The First Nordic Symposium on NMR Spectroscopy"

Some of the newsletter readers might be interested to know the date and venue of the First Nordic Symposium on NMR Spectroscopy which will take place on June 12-June 15th 1984 in Turku, Finland. The programme will consist of both basic problems and practical applications although the general theme will emphasize new applications rather than techniques. One invited lecture from each Scandinavian country will be included in addition to some keynote lectures, posters and possibly a couple of discussion groups. The keynote lectures will be selected (20 min. each) from the most novel topics offered by the potential participants. The participation will be limited to 100-120 people. The conference language will be English.

Nordic colleagues will get the first circular about this meeting through their departments and/or the local chemical papers (like Kemia-Kemi in Finland) but other interested readers should contact the undersigned as soon as possible.

Sincerely yours,

Kalevi Pihlaja, Professor  
Chairman, Section of NMR Spectroscopy, the Association of Finnish Chemical Societies

P.S. In mutual agreement with Professor Pekka Pyynkkä, I shall hereby take over his former subscription to the TAMU NMR Newsletter for the shared University of Turku - Abo Akademi NMR facility which by the way will in this year be a new multinuclear Jeol GX-400 system.
Buenos Aires, July 6, 1983.

Title: The Signs of the J's in Flurane.

Dear Prof. Shapiro:

The theoretical group of our local NMR team led by Prof. Ruben Contreras got used to bring us, experimentalists, some odd questions like e.g. "what is the relative sign of J_{AX} in an ABCX system in which J_{AX} is the only non-zero X coupling?"

Usually we do not mind their questions but what we do mind is their getting used to have us answering them!

The last question they brought us was: "what are the relative signs of J_{AX} and J_{MX} in flurane (formula shown) taking into account that, besides being this a degenerate system, J_{AM} = 0 ?!"

\[
\begin{align*}
(X) & \\
\text{Cl} & \text{F} & \text{H} & J_{AM} = 0 \\
(A) & \text{H} - \text{C} - \text{C} - \text{O} - \text{C} - \text{H} & \text{M} & J_{AX} = 4.45 \\
\text{Cl} & \text{F} & \text{H} & J_{MX} = 0.49
\end{align*}
\]

It took some brain-squeezing and some engineering work to be able to give them the answer, through a triple resonance experiment: "Both are the same!"

But we do hope that they are not going to ask us the absolute sign of these constants, since we are not so sure of being able to answer them that question!

Yours, sincerely

V. J. Kowalewski.

P.S. Thank's for the remainder!
Dear Professor Shapiro,

SOLID-STATE NMR SPECTRA OF THE ZEOLITE ZSM-5

Since our last contribution we have continued with our solid-state NMR work, studying all manner of nuclei, spinning at every imaginable angle, in as many different field strengths as possible.

In particular we have continued our work on organic ligands chemically bound to silica gel surfaces1 and have used 27Al magic angle spinning techniques at 130.3 MHz (11.75 T, Bruker WM-500 spectrometer) to characterize transitional aluminas2.

A suitable subject for this communication, however, would appear to be the 29Si NMR spectra of the zeolite ZSM-5, in which everyone seems to be interested.

In general, two types of 29Si ZSM-5 spectra have been published:

(a) a poorly resolved spectrum with Si(OAl) resonances centered around -113 ppm3, and

(b) a spectrum exhibiting a number of Si(OAl) resonances between -109 and -117 ppm4.

We have monitored the preparation and activation of such catalysts step-by-step using solid-state 29Si NMR5, and a typical example of our results (for a ZSM-5 having an initial Al content of 0.32 %w) is shown in the attached figure.
The spectrum of sample A in Figure 1 exhibits two broad resonances at -102 and -112 ppm. The -102 ppm resonance is due mainly to silanol groups (as shown by cross-polarization experiments, which we regard as essential in solid-state $^{29}$Si NMR studies), most of which are located inside the zeolite (lattice defects). As can be seen, upon calcination and ion exchange followed by further heat treatments, a better resolved spectrum is obtained. This is because silanol groups are removed by ring closure, which the presence of Na$^+$ and tetrapropylanmonium (TPA$^+$) ions otherwise inhibits. As a consequence of this final ring closure, the ZSM-5 lattice becomes more homogeneous, which is reflected by line narrowing in the spectrum, leading to the well-resolved spectrum of sample E in Figure 1.

We trust that this missive keeps our subscription open!

Yours sincerely,

KONINKLIJKE/ SHELL-LABORATORIUM, AMSTERDAM

(G.R. Hays) (N.C.M. Alma)


2) C.S. John, N.C.M. Alma and G.R. Hays, Appl. Catal. (in press). With thanks to Dr. A. Samoson (Tallinn, USSR) for the design and construction of the probe and help with carrying out the 130.3 MHz experiments, and to Bruker Analytische Messtechnik and Dr. W.E. Hull for the opportunity to use their WM-500 spectrometer in August 1982.


Encl.: 1 Figure
FIG. 1: $^{29}\text{Si}$ SOLID-STATE NMR OF ZSM-5

A. Na$^+$, TPA$^+$ ZSM-5 AFTER DRYING AT 120 °C
B. Na$^+$, H$^+$ ZSM-5 AFTER 500 °C CALCINATION OF A
C. NH$_3$$^+$, H$^+$ ZSM-5 AFTER Na$^+$ EXCHANGE OF B
D. H$^+$ ZSM-5 AFTER 500 °C CALCINATION OF C
E. H$^+$ ZSM-5 AFTER 800 °C HEAT TREATMENT OF D
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Department:_______________________________________________
Address:______________________________________________________
City/State/Zip:_____________________________________________
Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas. 77843
U.S.A.

Dear Barry:

Thank you for your reminders. The world is now falling back into its original place for me and I shall make a contribution along the lines of a comment on Ed Samulski's letter 297 19 (1983). In his last paragraph he alludes to the difficulty of incorporating deuteriated phospholipid in nematic solvents, but predicts an unchanged order profile for the lipid. In fact Bruce Forrest was able to get phospholipid guests in a lyotropic nematic host some years ago and similar profiles were obtained to biological situations. The results were published in Chem. Phys. Lipids 24 183 (1979). In comparing order profiles, it is possible to detect changes along the lines suggested by us in recent papers. Order profiles may look the same but in bilayer situations they are sensitive to the changes in bilayer thickness. Two recent papers from our laboratory illustrate this sensitivity of order profiles. J. Phys. Chem. 85 718 (1981) and J. Am. Chem. Soc. 105 1469 (1983).

We continue to work in the area of lyotropic aqueous cholesterics and nematics with NMR as the principal tool.

Yours sincerely,

Leonard W. Reeves,
Professor of Chemistry.

LWR/ee
Dear Barry,

When a strong d.c. electric field is applied over a polar liquid sample the molecules become partially oriented with their dipole-moments along the direction of the applied field. In the NMR spectrum anisotropic interactions between the spins will be manifest. In the case of (quadrupolar) \( I = 1 \) nuclei (e.g. \( ^{14}\text{N} \) and \( ^{2}\text{H} \)) the resonance-lines appear as doublets. The splitting \( \Delta v \) of a doublet depends on the nuclear quadrupole moment \( eQ \), the field-gradient along the dipole moment \( (V_{zz}) \) and the extent of orientation by the electric field (called the alignment, \( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \epsilon \)):

\[
\Delta v = \frac{3}{2} \frac{eQ}{h} V_{zz} \frac{3}{2} \cos^2 \theta - \frac{1}{2} \epsilon
\] (I)

Note that \( V_{zz} \) is the gradient in a molecular frame \((xyz)\), adapted to the symmetry of the molecule. The principal frame, in which the field gradient tensor is diagonal, is denoted by \((x'y'z')\). To express \( V_{zz} \) in the principal components, \( V_{x'x'} \), \( V_{y'y'} \) and \( V_{z'z'} \), an appropriate transformation has to be performed.

In deuterated pyridine (fig. 1a), in which the C-\( ^2\text{H} \) axis of the para-deuteron is along the dipole moment, \( V_{zz} \) is identical to \( V_{z'z'} \); the quadrupole coupling constant, \( \frac{eQ}{h} V_{z'z'} \), is known to be 186 kHz \((1)\). For the nitrogen spin \( V_z \) is also identical to \( V_{z'z'} \) (the field gradient along the lone pair). Then, from the ratio of the \( ^2\text{H} \) and \( ^{14}\text{N} \) line-splittings \( \frac{eQ}{h} V_{z'z'} \) for the nitrogen nucleus can be calculated \((-5.06 \text{ MHz})\). The situation in deuterated pyrimidine (fig. 1b) is identical as far as the oo- and mm-deuterons are concerned. For the nitrogen spins \( V_{zz} \) is a linear combination of the in-plane principal components:
Under the assumption that $^{14}$N principal field gradients are equal in magnitude and are oriented in the same way in the two molecules (i.e. $V_{z'z'}$ along the lone-pair, $V_{y'y'}$ perpendicular to the plane of the molecule) it is possible to solve eq. (II). The l.h.s. is given by the ratio of the $^{2}$H and $^{14}$N line-splittings in pyrimidine; in the r.h.s. $\frac{eQ}{h} V_{x'x'}$ is already known from the experiment on pyridine. $\frac{eQ}{h} V_{z'z'}$ can be calculated after substitution of the values for $\theta_{zx}$ and $\theta_{zz}$. The latter quantities can be derived from the molecular structure of pyrimidine (2) by identifying the bisector of the inner CNC-angle as the direction of the lone-pair (the $z'$-axis). The third principal component follows from the traceless character of the tensor.

The final results are: $\frac{eQ}{h} V_{x'x'} = +1.17$ MHz, $\frac{eQ}{h} V_{y'y'} = +3.89$ MHz and $\frac{eQ}{h} V_{z'z'} = -5.06$ MHz. The asymmetry parameter, $\eta$, is calculated to be 0.54.

From microwave data on pyridine, Sørensen (3) found the values +1.43, +3.45 and -4.88 MHz respectively, giving $\eta = 0.41$. Our value for $\frac{eQ}{h} V_{z'z'}$, -5.06 MHz is increased by about 10% compared to the crystal value from NQR (4). This behaviour has previously been found for nitrobenzene (5). There is reasonable agreement between the gasphase microwave data and the present results.

Sincerely yours,

C. MacLean  B.H. Ruessink  U. Hofstra

(3) G. Sørensen, J. Mol. Spectr. 22 (1967) 325.
Spectra of pyrimidine, deuterated at the o-o' and op-positions, in the presence of an electric field.
July 26, 1983

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

SUBJECT: MAGNETIC RESONANCE SPECTROSCOPIST  

Dear Dr. Shapiro:  

The Analytical Department at the Shell Development Westhollow Research Center in Houston, Texas has an opening for a PhD level magnetic resonance spectroscopist. The position will emphasize applications of multinuclear solution and solid-state NMR, NMR imaging and ESR in support of both oil and chemical R&D efforts. Applicants should have a firm grasp of the fundamentals of magnetic resonance. ESR experience is desirable. Qualified applicants should send resumes to:

Research Recruitment  
Shell Development Company  
P. O. Box 1380  
Houston, TX 77001

Yours truly,  

for M. J. O'Neal, Manager  
Analytical Department

TBM/pkm
July 26, 1983

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

Dear Barry,

Re: Self-Diffusion Measurements on the FX-90Q and Diffusion of Water in Planar Smectic Liquid Crystals.

Thanks for the multicolored reminders. Sorry we took so long to write. We would like to report some recent progress at Drexel in the measurement of self-diffusion coefficients. The technique used is the pulsed-gradient spin-echo (PGSE) method previously described by Stilbs (1,2) for FX series spectrometers. We have written a pulse program DIFUS which we believe to be an improvement over those previously reported. Since the sequence uses the homospoil accessory for the field gradient, no instrumental modification is necessary for FX-90Q owners with FG/BG and homospoil capability. In addition, one can, by adjusting the power to the coils gain a factor of about 4 in field gradient. We would be happy to share this program and write up of the experiment with your readers.

One example of work we have done using this technique is shown in the figure for the diffusion of water in smectic liquid crystals of the sodium 4-(1'-heptylnonyl) benzene sulfonate-(SHBS)-water system. In this system the water is believed to be in between planar bilayers separated by the 10Å water layer. The loop values shown are related to the amount of time the pulsed gradient is on. Shown as an inset is a plot of the ln(intensity) vs. $\beta^2$, where $\beta$ is related to the total echo time and pulsed gradient time (1,2). It is interesting to note that for this system it is possible to observe a water echo for an unoriented system and that the decay is clearly non-exponential (as observed in the inset). We are currently interpreting these results.

Sincerely,

E. Cheever

F. D. Blum

References:
Figure shows the echo attenuated water signal as a function of loop values (related to the field gradient pulse). Also shown is a plot of the intensity vs. $\beta$ (related to the echo time and field gradient pulse). The decay is clearly non-exponential.
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

DIETARY FIBER SORPTION AS PROBED BY $^{13}$C CPMAS NMR

Numerous animal and human feeding studies suggest that "non-nutritive" dietary fiber binds bile acids in the gut and thereby initiates a biochemical cascade which ultimately reduces serum cholesterol levels.

In our recent investigations of the characterization and interactions of dietary fibers, we examined the dynamics of bile acid sorption to the surface of insoluble vegetable (fiber) via $^{13}$C CPMAS NMR.

Alcohol insoluble dietary fibers composed primarily of polysaccharides containing neutral saccharides i.e., glucose, arabinose, mannose and galactose, (~70%), and uronic acid residues, (~20%), are incubated with solutions containing 95% $^{13}$C$_{24}$O enriched cholate at pH 7.3. After a thorough washing, these fibers were examined by $^{13}$C CPMAS as a function of proton T$_1$ spin lattice relaxation times. Figure 1 shows the proton relaxation profile via the carbon resonances of the polysaccharide fiber from carrot with approximately three weight percent physically sorbed cholate. The sharp carbonyl resonances seen at 177 and 183 ppm correspond to the protonated and ionic forms of the sorbed cholic acid, respectively. While the pure amorphous cholate has a proton T$_1$ of 192 ms and the protonated form a value of 62 ms, the physically bound cholic acid (found in both states), have an average T$_1$ value of 485 ms. Crystalline cholic acid has a T$_1$ value of 1200 ms. The rapid proton spin diffusion throughout the fiber gives a uniform proton T$_1$ value for all the polymer carbons of 172 ms.

Similar measurements made for cholate ionically linked to cholestyramine (a cross linked polystyrene polymer containing quaternary amine exchange sites) clearly demonstrated rapid mutual spin diffusion between the synthetic polymer proton and cholate proton pool to yield a common proton T$_1$ of 140 ms.

From these experimental results it is evident that the fiber matrix provides structural rigidity for the bile acid, in both the protonated and ionic states aligned on the surface or perhaps within the fiber matrix.

It is obvious from this result that $^{13}$C CPMAS NMR is a useful tool for evaluating the nature of small molecule-polymer interactions.

PHILIP E. PFEFFER
Research Leader
Physical Chemistry and Instrumentation Laboratory

PETER D. HOAGLAND
Research Chemist
Food Science Laboratory
CARROT RESIDUE WITH 3% SORBED $^{13}$C$_{24}$ CHOLATE pH = 7.3

$T_{1H}$ INVERSION-RECOVERY

$T_{1H}$
BOUNDED CHOLATE - 485 ms ± 10%
FIBER - 172 ms ± 10% Ave.
AMORPHOUS CHOLATE - 192 ms ± 10%
AMORPHOUS CHOLIC ACID - 63 ms ± 10%

200 100 0
PPM
July 28, 1983

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

Dear Professor Shapiro:

Please excuse my too-long silence. We find ourselves in the perhaps enviable position of having several NMR's, all at different field strengths. This poses an annoying problem for those who want to measure probe temperatures using either CH₃OH or (CH₂OH)₂ shifts, as the published calibration curves are for 60 MHz instruments. Your readers may find the following two equations useful in similar situations:

For CH₃OH - \[ T = 403 - \frac{29.5 \{\Delta \nu\}}{M} - \frac{23.81 \{\Delta \nu\}^2}{M^2} \]

For (CH₂OH)₂ - \[ T = 466.4 - \frac{100.5 \{\Delta \nu\}}{M} \]

where \( T \) is temperature in degrees K  
\( M \) is field strength in MHz  
\( \Delta \nu \) is chemical shift difference in Hz

Sincerely,

Mary W. Baum

Mary W. Baum
July 25, 1983

Dear Barry:

Below is an announcement for a position in the Colorado State University Regional NMR Center. We hope that some of the Newsletter's readers might be interested.

**NMR SPECIALIST**

COLORADO STATE UNIVERSITY NMR CENTER

Research Associate position in the NSF-sponsored regional instrumentation facility in nmr. Position available by December 1, 1983.

**REQUIREMENTS:** Advanced degree in chemistry, physics or electrical engineering. Strong preference for applicants experienced in modern nmr techniques, especially for solids.

**SALARY:** Negotiable, dependent upon qualifications and experience.

**APPLICATION DEADLINE:** September 15, 1983.

Send applications with complete resume, including publications, three references and statement of interests to:

Professor Gary E. Maciel
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

Progress in the Center has focussed recently on solid-state NMR applications in a variety of areas. For example, we have been very happy with the information we have been able to get from $^{15}$N CP/MAS experiments regarding the interactions of amines with surfaces. We are also beginning to get useful MAS data on $^{109}$Ag.

Sincerely,

Gary E. Maciel
Professor
EAS announces for the NMR spectroscopists a day of advances in this rapidly expanding field with the following program scheduled for Thursday, November 16, 1983:

**Advances in NMR**: Chairperson, Dr. Gwendolyn N. Chmurny, Frederick Cancer Research Facility, 9:00 a.m. to 12:00 noon,

1. Dr. Roy H. Bible, Jr., G.D. Searle Company
   "An Introduction and Overview of Two-Dimensional High-Resolution NMR Spectroscopy"

2. Dr. Robert E. Santini, Purdue University
   "A Technical Review of High Field NMR Spectrometer Capabilities with a Projection of Future Developments in Biomedical Applications"

3. Dr. Robert S. Balaban, National Institutes of Health
   "Two-Dimensional NMR Studies of Enzymatic Reactions in Vitro and in Vivo"

**Advances in NMR Imaging**: Chairperson, Prof. Paul C. Lauterbur, 2:00 p.m. to 4:30 p.m.

1. Prof. Paul C. Lauterbur, State University of New York at Stony Brook
   "NMR Zeugmatographic Imaging of Solids, Liquids and Gases"

2. Dr. Ian L. Pykett, Massachusetts General Hospital
   "NMR Chemical Shift Imaging"

3. Dr. W.P. Rothwell, Shell Development Company
   "Industrial Applications of NMR Imaging"

This is part of the Twenty-Second Eastern Analytical Symposium, November 16-18, 1983. For further information, contact Dr. S. David Klein, EAS Publicity, Merck and Company, Inc., P.O. Box 2000, R80 L106, Rahway, NJ 07065.

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Complete computer control
The QE-300 makes it possible for virtually anyone to get high quality NMR spectra—quickly and easily—without previous training or NMR experience. A powerful NMR software package lets you set up and automate sample runs to your own criteria. And since the software is completely menu-driven, it's almost impossible to make a mistake.

All an operator has to do is slip a sample in and type a single key on the control console. The computer controls the spin rate, magnet shimming, lock frequency, and spectral phasing, acquires data to preset default parameters, and prints out the results, complete with full annotation of system settings.

You don't even have to change probes to get carbon and hydrogen spectra on the same sample. Just enter a single command, and the QE-300 makes the 1H to 13C conversion automatically.

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The QE-300 has features that make it a pleasure to use, too. Like a color display, an eight-pen color plotter, and a dual floppy disc system for interactive spectral analysis and unlimited external data storage.

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