MASTER

THE CHEMICAL SHIFT ANISOTROPIES OF ^1H IN
 $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, AND $\text{C}_6\text{H}_6(\text{s})$

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The chemical shift anisotropies of ^1H in
 $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, and $\text{C}_6\text{H}_6(\text{s})$

by

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ABSTRACT

The proton NMR in powdered samples of $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, and $\text{C}_6\text{H}_6(\text{s})$ have been studied by multiple pulse line narrowing techniques. The resultant spectra provide nuclear magnetic shielding tensors that are (at least approximately) axially symmetric. The anisotropy, $\Delta\sigma = \sigma_{\perp} - \sigma_{\parallel}$, is 34.2 ± 1.0 ppm for ice, 11.1 ± 1.0 ppm for the highest-temperature phase of solid hydrogen sulfide, and -5.3 ± 0.3 for benzene. Comparisons are made with previous experimental and theoretical work.

I. INTRODUCTION

The effect of the electronic environment of a nucleus upon its magnetic resonance frequency, first discovered in 1950 by Proctor and Yu (1), can be described by a symmetric, second-rank tensor, $\bar{\bar{\sigma}}$. The usefulness of this quantity is in its sensitivity to the anisotropy of the electronic environment around a nucleus. That is, the chemical shift is directly related to molecular structure (2). In conventional high resolution NMR measurements on liquids, because of rapid molecular reorientation, only the isotropic part of $\bar{\bar{\sigma}}$ is accessible, or

$$\bar{\sigma} = \frac{1}{3}\text{Tr}(\bar{\bar{\sigma}}) = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad . \quad (1)$$

The σ_{ii} are the principal components of $\bar{\bar{\sigma}}$. While the utility of this parameter is beyond contention, considerably more information is available from a knowledge of the individual quantities that characterize $\bar{\bar{\sigma}}$ (3, 4).

In order to gain experimental access to the principal components of $\bar{\bar{\sigma}}$, one requires a state, unlike the liquid, in which random motion takes place in a time scale long compared to that of the NMR experiment. One example of such a state is the solid state. However, the NMR spectra of solids are typically broad due to internuclear dipole-dipole interactions (which are averaged to zero in liquids), and again

the full chemical shift information is hidden.

For a few nuclei, such as ^{31}P , the large chemical shifts and small dipolar broadening do permit the solid state spectra to be analyzed without using special methods (5). It is only with the development of multiple pulse NMR techniques (6-8) to suppress dipolar broadening that it has become possible to determine chemical shift anisotropies in solids with strong homonuclear dipolar coupling. Other methods, such as "second moment" analysis (9), and NMR of solids partially oriented in liquid crystals (10-12) have been found to be generally unreliable. Thus, using single crystals of known structure, it becomes possible to specify the full symmetric, second-rank $\bar{\sigma}$ tensor. This would involve a specification of the chemical shielding along three orthogonal directions and the angles relating this system to the molecular coordinate system. Where powder samples are employed, only the values of the three "principal components" of $\bar{\sigma}$ are obtained, their orientation relative to the molecule being lost.

Whereas multiple pulse techniques have made possible the measurement of chemical shift tensors of ^{19}F and ^{13}C in many compounds, this state of affairs has been persistently less true for ^1H . Relative to ^1H , fluorine shielding anisotropies (the difference between two particular components) are large, around 200 ppm (13), and the dipolar broadening

relatively smaller, so that resolution requirements are less severe. Nuclei such as ^{13}C , by virtue of their low isotopic abundance, require, at most, the simpler method of strong heteronuclear decoupling (14) to furnish highly resolved spectra. In detailing chemical shift anisotropies of protons in solids, however, one must contend with the strongest dipolar coupling between nuclei, and the smallest chemical shift anisotropies. Typically these are 20-60 KHz and 1.7 KHz, respectively (3), for a spectrometer operating at 56 MHz. This "serious challenge to multiple pulse techniques" was noted by Pines et al. (15) in presenting their method of isotopic dilution with ^2H , and deuterium spin decoupling as the simplest method for obtaining chemical shift information in such systems.

It is the purpose of the studies presented in this work to show that isotopic dilution (15) is not necessary to obtain chemical shift information in solids with large homonuclear dipolar coupling, and, using multiple pulse techniques, to measure the principal components of the chemical shift tensor in three systems of experimental and theoretical interest, ice, hydrogen sulfide, and benzene.

II. THEORY

A. Basic Theory

Nuclear magnetic resonance (NMR) is a technique for studying nuclear spin environments using the absorption of radio frequency energy as a probe. The method was first developed in 1946, at Harvard, by Purcell, Torrey, and Pound (16), and independently at Stanford by Bloch, Hansen, and Packard (17). Because the background and details are well-known (18, 19), only a brief review is given.

A nucleus with spin $\vec{I}$ has a magnetic moment given by

$$\vec{\mu} = \gamma \hbar \vec{I} \quad , \quad (2)$$

where γ , the gyromagnetic ratio, is a constant for a given nucleus. A magnetic moment placed in a magnetic field H_0 , directed along the z axis, will have an interaction described by the Zeeman Hamiltonian

$$\mathcal{H}_Z = - \vec{\mu} \cdot \vec{H}_0 = - \gamma \hbar \vec{I} \cdot \vec{H}_0 = - \gamma \hbar I_z H_0 \quad . \quad (3)$$

The eigenvalues of this system are

$$E = - \gamma \hbar H_0 m \quad , \quad (4)$$

where m , the magnetic quantum number, can have the values $I, I-1, \dots -I$. Thus, the energy separation between levels is

$$\Delta E = - \gamma \hbar H_0 = \hbar \omega \quad (5)$$

The selection rule for transitions between energy levels is $\Delta m = \pm 1$, and in nuclear magnetic resonance, transitions are induced between these levels by application of a radio-frequency field, H_1 , perpendicular to H_0 with a frequency

$$\vec{\omega}_0 = - \gamma \vec{H}_0 \quad (6)$$

called the Larmor frequency.

B. Relaxation Phenomena

It is also important to explain two characteristic times connected with NMR. Consider for a moment a collection of nuclear spins in thermal equilibrium with one another in a strong static magnetic field, H_0 . Such nuclei will be distributed among the $2I + 1$ nuclear spin energy levels according to the Boltzmann distribution. This results in a net magnetization in the direction of the applied field (again taken to be the z direction), $M_z = M_0$. Suppose this system is disturbed in such a way as to leave $M_y = M_0$ and $M_{x,z} = 0$ (as is often done in practice). The characteristic time for the exponential decay of the nuclear spin system toward thermal equilibrium within itself is called the spin-spin (or transverse) relaxation time, T_2 (18). T_1 , called the spin-lattice (or longitudinal) relaxation time,

is the characteristic time of the spin system to approach thermal equilibrium with the lattice or heat bath which is comprised of the remaining degrees of freedom (electronic, translational, etc.) (18).

C. The Chemical Shift Tensor

From Equation 6, it is seen that the resonant frequency of a particular nucleus depends on the magnetic field it experiences. For a nucleus in a molecule, the "effective field", $\vec{H}_0 + \vec{H}'$, is different from the applied field due to shielding by the electrons around the nucleus. We can write

$$\vec{H}' = - \bar{\sigma} \vec{H}_0, \quad (7)$$

where $\bar{\sigma}$ is the magnetic shielding tensor. The resonant frequency, then, is

$$\vec{\omega} = - \gamma (\vec{H}_0 + \vec{H}') \quad (8)$$

$$= - \gamma (\bar{I} - \bar{\sigma}) \cdot \vec{H}_0. \quad (9)$$

The Hamiltonian for the chemical shift, which is just a modification to the Zeeman interaction is

$$\mathcal{H}_\sigma = - \gamma \hbar \bar{I} \cdot \bar{\sigma} \cdot \vec{H}_0. \quad (10)$$

The shielding tensor defined by Equation 7 is a tensor with nine components,

$$\sigma_{ij} = \begin{vmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{yz} & \sigma_{zz} \end{vmatrix}, \quad (11)$$

so that, e.g.,

$$H'_x = (\sigma_{xx}H_x + \sigma_{xy}H_y + \sigma_{xz}H_z) \quad , \quad (12)$$

etc. Because $\bar{\sigma}$ is symmetric ($\sigma_{ij} = \sigma_{ji}$) only six of these components are, in fact, different. This tensor can be diagonalized so that it has only the three diagonal elements, σ_{xx} , σ_{yy} , and σ_{zz} different from zero. Because the electronic environment about a nucleus in a molecule is generally anisotropic, these "principal components" are usually not all equal. This is given explicitly in Ramsey equation (20), which provides the basis for theoretical calculations of chemical shift tensors:

$$\begin{aligned} \sigma_{zz} = & \frac{e^2}{2mc^2} \langle 0 | \sum_i \frac{(x_i^2 + y_i^2)}{r_i^3} | 0 \rangle \\ & - \frac{e^2 \hbar^2}{2m^2 c^2} \sum_{n>0} (E_n - E_0)^{-1} [(\langle 0 | \sum_i L_{zi} | n \rangle) (\langle n | \sum_i \frac{L_{zi}}{r_i^3} | 0 \rangle)] \end{aligned}$$

$$+ (\langle 0 | \sum_i \frac{L_{zi}}{r_i^3} | n \rangle) (\langle n | \sum_i L_{zi} | 0 \rangle)] \quad (13)$$

with similar expressions for the xx and yy components. e and m are the electron charge and mass, c is the speed of light, $\langle 0 |$ indicates the ground state wave function, the sum over i is over all electrons, the sum over n is over all excited states, L_{zi} is the orbital angular momentum operator of the i^{th} electron in the z direction, the origin of the x , y , and z axes is at the nucleus in question, and r_i is the distance from the nucleus to electron i . As seen above, Ramsey separated the chemical shift tensor into two terms. The first term is positive and is known as the diamagnetic contribution to $\bar{\sigma}$. The second term is of opposite sign and is called the paramagnetic contribution.

The diamagnetic term involves only ground state wave functions, whereas the paramagnetic term involves a summation over all excited states. Thus, an exact calculation of $\bar{\sigma}$ from Equation 13 is not possible, as knowledge of the excited state wave functions is normally not available. Approximate methods of estimating the paramagnetic term have been developed (21-24) and a great number of ab initio approaches (25-27) exist, but the evaluation of Ramsey's formula remains a difficult problem.

1. Powder spectrum lineshapes

Experimental methods for determining shielding anisotropies were mentioned briefly in Chapter I. In this work, only studies of powdered solids were attempted, so only the principal elements of $\bar{\sigma}$ could be measured. This is because with powders there is a random distribution of orientations of the crystalline axes, and the resultant lineshape is a sum of the individual contributions (4, 28).

Figure 1 shows the theoretical powder spectrum lineshape for the general case where $\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$. In the case of axial symmetry, where two of the components are equal, the lineshape appears as in Figure 2. The principal shielding components can be obtained from an experimental powder spectrum by fitting it with a theoretical pattern convoluted with a broadening function (Gaussian or Lorentzian) to account for residual broadening. A computer program to do this for the axially symmetric case is given in the Appendix.

D. Multiple Pulse NMR Techniques

There are basically two ways that nuclear magnetic resonance can be observed in bulk materials (29); the continuous wave method or the pulse method. In the conventional pulse method the spin system is subjected to a short intense burst, or "pulse", of rf power that rotates the

Figure 1. The theoretical powder line shape for an arbitrary chemical shift tensor. The full curve gives the experimental line shape where residual broadening is superimposed

Figure 2. The theoretical and experimental line shapes for an axially symmetric chemical shift tensor

magnetization away from its equilibrium position. Then, while M_z relaxes back to M_0 , the transverse components make up a rotating magnetic moment which induces a signal in a detector. The observed signal, $A(t)$ vs t , called a free induction decay (FID), is the inverse Fourier transform of the cw spectrum, $A(\omega)$ vs ω (18, 30), so that the same information is contained in either representation.

In solids, as mentioned before, the NMR spectra are dominated by dipolar interactions, so that neither the continuous wave nor single pulse experiments yield much information about smaller, more chemically interesting interactions such as chemical shifts. However, with recent developments in multiple pulse experiments (6-8) it has been shown that the application of cyclic trains of rf pulses are capable of altering spin interactions so that the dipolar broadening can be selectively removed, revealing the hidden structure. Thus, the Fourier transform of these multiple pulse experiments is the conventional frequency spectrum that would be obtained from a system in which the dipolar broadening had been removed and the chemical shifts had been scaled by some measurable constant.

1. Average Hamiltonian Theory

The basic theory underlying multiple pulse NMR experiments, called Average Hamiltonian Theory, has been developed

by Waugh and others (6, 31-36). The starting point is a description of the nuclear spin system in terms of the density matrix, ρ (19). In a pulse experiment, the signal detected is proportional to a component of the nuclear spin angular momentum operator, $\vec{I}$, in the xy plane (37), or

$$\langle I_x(t) \rangle = \text{Tr}(\rho(t) I_x) \quad . \quad (14)$$

Thus, if the spin system is subjected to a train of rf pulses, the time development of the spin system is describable in terms of the time evolution of the density matrix. The equation of motion for the evolution of the density matrix is (31)

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] \quad , \quad (15)$$

where $\mathcal{H}$ is the spin Hamiltonian. In the interaction frame of the Zeeman interaction (i.e., the rotating frame) $\mathcal{H}$ can be written as

$$\mathcal{H}(t) = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{rf}}(t) \quad (16)$$

where

$$\mathcal{H}_{\text{int}} = \mathcal{H}_0 + \mathcal{H}_\sigma + \mathcal{H}_D^{(z)} \quad . \quad (17)$$

$\mathcal{H}_0$ is the offset Hamiltonian, $\mathcal{H}_\sigma$ the chemical shift, and $\mathcal{H}_D^{(z)}$ the truncated dipolar interaction; in frequency units, we have

$$\mathcal{H}_0 = -\gamma(\omega_0 - \omega)I_z \quad (18)$$

$$\mathcal{H}_\sigma = -\omega_0 \sum_i \sigma_{zzi} I_{zi} \quad (19)$$

$$\mathcal{H}_D^{(z)} = \sum_{i < j} \sum b_{ij}(\vec{r}_{ij})(\vec{I}_i \cdot \vec{I}_j - 3I_{iz}I_{jz}) \quad (20)$$

where i and j refer to the individual spins, and ω_0 is the Larmor frequency defined by Equation 6. $\mathcal{H}_{rf}$ is the Hamiltonian for the interaction between the nuclear spin system and the pulse train, and so, depends on the particular pulse sequence used.

It can be shown (31, 38) that the solution of Equation 15 may be written in terms of the density matrix $\rho(o)$, at some initial time $t = o$, as:

$$\rho(t) = U(t,o)\rho(o)U(t,o) \quad (21)$$

where

$$U(t,o) = U_{rf}(t,o)U_{int}(t,o) \quad (22)$$

with

$$U_{rf}(t,o) = T \exp\left[-i \int_o^t \mathcal{H}_{rf}(t')dt'\right] \quad (23)$$

and

$$U_{int}(t,o) = T \exp\left[-i \int_o^t \tilde{\mathcal{H}}_{int}(t')dt'\right] \quad (24)$$

and

$$\tilde{\chi}_{\text{int}}(t) = U_{\text{rf}}^{\dagger}(t,0) \chi_{\text{int}} U_{\text{rf}}(t,0) \quad . \quad (25)$$

T is the Dyson time ordering operator, meaning that Equations 23 and 24 are extremely complicated for an arbitrary $\chi_{\text{rf}}(t)$. However, simplifications occur by using a pulse sequence which is both periodic and cyclic, i.e.

$$\chi_{\text{rf}}(t + Nt_c) = \chi_{\text{rf}}(t) \quad (\text{periodic}) \quad (26)$$

$$\int_0^{Nt_c} \chi_{\text{rf}}(t) dt = 0 \quad , \quad (\text{cyclic}) \quad (27)$$

and by restricting observation of the spin system to integral multiples of the cycle time, t_c (35). From Equations 23 and 27,

$$U_{\text{rf}}(Nt_c,0) = T \exp(0) = 1 \quad , \quad (28)$$

and then

$$U_{\text{int}}(Nt_c,0) = [U_{\text{int}}(t_c,0)]^N \quad . \quad (29)$$

Now $U(Nt_c,0)$ can be expanded using the Magnus formula (39),

$$U_{\text{int}}(Nt_c,0) = \exp[-iNt_c(\bar{H}_{\text{int}}^{(0)} + \bar{H}_{\text{int}}^{(1)} + \bar{H}_{\text{int}}^{(2)} + \dots)] \quad , \quad (30)$$

where

$$\bar{H}_{\text{int}}^{(0)} = \frac{1}{t_c} \int_0^{t_c} \tilde{H}_{\text{int}}(t') dt' \quad (31)$$

$$\bar{H}_{\text{int}}^{(1)} = \frac{-i}{2t_c} \int_0^{t_c} dt'' \int_0^{t''} dt' [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')] \quad (32)$$

$$\bar{H}_{\text{int}}^{(2)} = \frac{1}{6t_c} \int_0^{t_c} dt''' \int_0^{t'''} dt'' \int_0^{t''} dt' \{ [\tilde{H}_{\text{int}}(t'''), [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')]] + [\tilde{H}_{\text{int}}(t'''), [\tilde{H}_{\text{int}}(t'), [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')]]] \} \quad (33)$$

The strong condition for convergence at this series is

$$t_c \|\tilde{H}_{\text{int}}(t)\| \ll 1 \quad (34)$$

At times $t = Nt_c$, then, the density matrix behaves as if it develops under an "effective" Hamiltonian

$$\bar{H}_{\text{int}} = \bar{H}_{\text{int}}^{(0)} + \bar{H}_{\text{int}}^{(1)} + \bar{H}_{\text{int}}^{(2)} + \dots \quad (35)$$

which is time independent. By our choice for χ_{rf} , we can thus control the Hamiltonian under which the spin system appears to evolve, and obtain results which are quite

different from conventional NMR experiments. In the limit of short t_c , the higher order correction terms vanish, and this Hamiltonian just becomes $\bar{H}_{int}^{(0)}$, called the "average" Hamiltonian.

2. The eight pulse cycle

Most applications of the theory outlined above have been in the development of pulse sequences which will remove or attenuate the dipolar broadening in solids (6-8). One such sequence is the REV-8 pulse cycle (8) shown in Figure 3. The average Hamiltonian for the eight pulse cycle, assuming an H_{int} given by Equation 17, is (40)

$$\bar{H}_{\Delta\omega}^{(0)} = \frac{1}{3} \sum_i (\Delta\omega) [(1+2a)(I_{xi} + I_{zi}) - \epsilon_i I_{zi}] \quad (36)$$

$$\bar{H}_{\sigma}^{(0)} = \frac{1}{3} \sum_i (\omega_o \sigma_{zzi}) [(1+2a)(I_{xi} + I_{zi}) - \epsilon_i I_{zi}] \quad (37)$$

$$\bar{H}_D^{(0)} = 0 \quad (38)$$

$$a = \frac{3t_w}{t_c} \left(\frac{4}{\pi} - 1 \right), \quad (39)$$

where the effect of finite pulse length error, ϵ_i , and finite pulse width, t_w , have been taken into account. As can be seen, the average Hamiltonian has no contribution from the dipolar Hamiltonian to first order. The effective

Figure 3. REV-8 pulse cycle

field is pointing along the $[101]$ direction, and so the chemical shift and resonance offset will be scaled by $\sqrt{2} (1+2a)/3$. In Figure 3, P_x refers to a rotation of the magnetization by 90° about the x axis in the rotating frame, and $\tau = t_c/12$.

III. EXPERIMENTAL METHODS

A. The Equipment

The pulse NMR spectrometer used in these experiments was similar to those of Ellett et al. (41) and Vaughan et al. (42), and has been described elsewhere (43). The block diagram is shown in Figure 4. It is a single sideband unit capable of broadband operation, operating at a frequency of 56.5 MHz for protons. A deuterium lock stabilized the spectrometer to within 10 Hz to permit signal averaging. The pulse programmer allowed for the utilization of any sequence of up to 24 pulses in four channels, differing by an adjustable rf phase. The transmitter was an IFI model 404 distributed amplifier system, capable of 500 watts in pulsed operation. With proper matching of transmitter to probe, and a probe Q of 45, $\pi/2$ pulses could be generated in 1.25 microseconds. Total dead time between turn off of pulse entering the power amplifier and reception of undistorted NMR signal was 1.5 microseconds, of which all but 10 nanoseconds was associated with probe ring-down. Briefly, the receiver consisted of three stages, the first two being Spectrum Microwave Model SMLD-10 limiting amplifiers, and the third being an Avantek Model UTO-50L amplifier. The unit was tuned to the operating frequency by inserting series tuned LC circuits between the first and second, and second and third stages. The transient recorder was a

Figure 4. Schematic of the pulsed nuclear magnetic resonance equipment

Biomation 805, with minimum sampling time of 0.2 microseconds per channel. The memory of the unit contains 2048 eight bit words. The Biomation is interfaced to a PDP 11/10 computer for signal averaging and data manipulation.

The homogeneity of the H_1 field is indicated by the decay (8) in Figure 5, taken on a sample of water. The figure exhibits the response to $128 \pi/2$ pulses over a time scan of 100 msec.

B. Experimental Procedure

The pulse sequence used was the REV-8 pulse sequence (8) which removes homonuclear dipolar interactions to second order and minimizes experimental artifacts relative to the WAHUHA 4-pulse cycle (6). The tuning procedure for multiple pulse experiments has been given in detail elsewhere (42) and will not be repeated. Spectra of both ice and solid H_2S were measured relative to liquid water at room temperature. The temperature of the solids was $-100^\circ C$, controlled to within $\pm 2^\circ C$ with a Varian V-4343 NMR Variable Temperature Controller. Temperature was measured with a chromel-alumel thermocouple. Spectra of solid benzene were obtained at $-50^\circ C$, $-100^\circ C$, and $-188^\circ C$, referenced to the liquid at room temperature. Solid hydrogen sulfide was prepared from commercial gas by condensation in an evacuated tube submerged in liquid nitrogen. This tube was then transferred to the

Figure 5. The response of protons to 128 $\pi/2$ pulses. The total scan shown is 100 msec

NMR probe at -100°C . Powdered ice and benzene were obtained simply by freezing the liquid standard in the probe. In all cases the samples were contained in standard 5 mm NMR tubes and were less than 5 mm in length.

A free induction decay of ice at -100°C was characterized by a T_2^* of $9.4 \mu\text{sec}$, and is shown in Figure 6. T_2^* is the transverse relaxation time plus an instrumental contribution due to magnetic field inhomogeneity. The strong convergence criterion for choosing a multiple pulse cycle time which will average a given interaction is

$$t_c = ||\tilde{H}_{\text{int}}(t)|| \ll 1 \quad . \quad (34)$$

$||\tilde{H}_{\text{int}}(t)||$ is the magnitude of the internal interaction in the frame of the rf signal. Thus, if

$$||\tilde{H}_{\text{int}}(t)|| \approx (\pi T_2^*)^{-1} \quad , \quad (40)$$

the criterion for multiple pulse narrowing of the proton spectrum in ice is $t_c \ll 30 \mu\text{sec}$. A value of $t_c = 27.6 \mu\text{sec}$ was found to be sufficiently short for removal of dipolar broadening in $\text{H}_2\text{O}(\text{s})$ and also in $\text{H}_2\text{S}(\text{s})$ and $\text{C}_6\text{H}_6(\text{s})$.

T_1 for the highest-temperature phase of solid H_2S is known to be quite short (44), and the 10 seconds allowed for spin-lattice recovery was more than enough to accommodate the usual $5 T_1$ (37). Ice, on the other hand, has a long T_1

Figure 6. A free induction decay of ice at -100°C . The total scan shown is $100\ \mu\text{sec}$

(45), and it is doubtful if this condition was ever satisfied in this system. In varying the sampling rate from 300 to 1000 seconds, however, no change was observed in the decay or subsequent Fourier transform frequency spectrum. In benzene at -50°C and -100°C , T_1 is again short (46) and the sampling time was 15 sec. At -188°C , however, T_1 increases to about 1000 seconds (46). The procedure used in this case was to melt the sample between scans and allow the magnetization to reach equilibrium in this state (where T_1 was much shorter) before refreezing.

At the beginning of each experiment, calibration markers spaced 1KHz apart were generated using a liquid sample, as illustrated by Figure 7. These markers allowed a determination of the chemical shift scaling factor (8). The value of the scaling factor in the present experiments may be estimated by a consideration of the average Hamiltonian under the REV-8 sequence, taking into account only finite pulse widths.

$$\bar{H} = \frac{1}{3} \sigma \left[1 + \frac{6t_w}{t_c} \left(\frac{4}{\pi} - 1 \right) \right] [I_z + I_x] \quad (41)$$

where t_w is the pulse length for a $\pi/2$ pulse. Ignoring phase transient effects and H_1 inhomogeneities, then, the scaling factor is

Figure 7. Liquid chemical shift markers spaced 1 KH_z apart

$$S = \frac{\sqrt{2}}{3} \left[1 + \frac{6t_w}{t_c} \left(\frac{4}{\pi} - 1 \right) \right] . \quad (42)$$

The pulse width in the present experiments was $1.25 \mu\text{sec}$, so that the anticipated reciprocal of the scaling factor, for a cycle time of $27.6 \mu\text{sec}$, is 1.98. In the present measurements, the experimental scaling factor was determined to be 1.98 ± 0.03 .

IV. RESULTS AND DISCUSSION

A. $\text{H}_2\text{O}(\text{s})$

Figure 8 shows the powder spectrum of ^1H in ice. The crosses are experimental points. The solid curve is a computer fit for an axially symmetric chemical shift tensor convoluted by a Lorentzian broadening function (47), 280 Hz in width. It is seen that the shielding is approximately axially symmetric, as is the general case for protons in hydrogen bonds (3, 4). The principal values furnished by a statistical best fit of the theoretical line are $\sigma_{\perp} = -6.5 \pm 0.6$ ppm and $\sigma_{\parallel} = +27.7 \pm 1.0$ ppm relative to liquid water. There is a ± 0.3 ppm uncertainty in the placement of the reference shift, so that the indicated chemical shift anisotropy ($\sigma_{\parallel} - \sigma_{\perp}$) is 34.2 ± 1.0 ppm. There is an isotropic shift of 4.8 ± 0.7 ppm from liquid water. This value for the overall anisotropy compares favorably with the value of 34 ± 4 ppm obtained in reference 15. The principal values and the isotropic shift are, however, significantly different. Unfortunately, the authors did not say what bulk susceptibility corrections were or were not made, so it is not possible to make absolute comparisons with the present data.

Theoretical studies of the magnetic shielding in protons hydrogen bonded to oxygen are also available (48, 49). In these studies, the unique axis of the σ tensor is found

Figure 8. Multiple pulse NMR powder spectrum of ^1H in $\text{H}_2\text{O(s)}$ at -100°C relative to liquid water

to be parallel to the hydrogen bond, a result also characteristic of single crystal studies (3). For an H-O.....H separation of 2.76 Å, as in ice (50), the recently published ab initio calculation by Ditchfield (48) suggests that the anisotropy in the chemical shift tensor should be about 33 ppm. Lau and Vaughan (49), using a different approach, separate the chemical shift tensor into "geometrical" and "chemical" contributions, where "geometrical" refers to the relative positions of the nuclei in a molecule, and "chemical" to the electronic interactions associated with chemical bonding. For an O-H.....O separation of 2.7 Å, these authors plot the purely geometrical contribution to the anisotropy in the chemical shift vs. the O-H bond distance. For ice, in which the O-H separation is 1.01 Å (50), their model predicts this contribution to be roughly 33 ppm. Thus, the present data suggest that the tensor is determined almost entirely by the geometry of the hydrogen bond.

B. H₂S(s)

The proton spectrum of hydrogen sulfide at 173 K is shown in Figure 9. Hydrogen sulfide at atmospheric pressure solidifies at -85.6°C and undergoes phase transitions at -147.0°C and 169.7°C. Whereas there is some evidence for hydrogen bonding in the low-temperature tetragonal phase

Figure 9. ^1H powder spectrum of $\text{H}_2\text{S(s)}$ at -100°C relative to liquid water

(51), the higher-temperature phases are generally thought to be molecular solids in which the molecules are bound together by van der Waals' forces (44, 51). The Lorentzian broadening function used to fit the spectrum in Figure 9 was 350 Hz wide. The principal values obtained were $\sigma_{\perp} = -10.0 \pm 0.8$ ppm and $\sigma_{\parallel} = +1.1 \pm 0.8$ ppm relative to room temperature water. Again, a portion of the uncertainty is in the reference sample, and so, the total anisotropy in the chemical shift is 11.1 ± 1.0 ppm. It was not found necessary to correct the values for bulk susceptibility effects.

This is the first determination of the chemical shift tensor of a hydrogen bonded to sulfur. No theoretical calculations exist for the chemical shielding in H_2S . It is not possible at this time, then, to draw conclusions about the nature of the bonding in $\text{H}_2\text{S(s)}$ from this measurement. Data on hydroxyl protons have shown the anisotropy in the shielding tensor to be much larger in the hydrogen bonded case than in the nohydrogen bonded case. Further studies of chemical shielding tensors in S-H bonded systems, including species where hydrogen bonding to sulfur is thought to exist (52), may hopefully reveal a similar correlative relationship.

C. $C_6H_6(s)$

At temperatures above $-188^{\circ}C$, benzene molecules are known to rotate rapidly about their six-fold axes (46, 53). This motion results in the components of the shielding tensor perpendicular to the rotation axis being averaged, forcing the shielding tensor to be axially symmetric. This is seen in Figure 10, which shows the powder spectrum of 1H in C_6H_6 at $-50^{\circ}C$. The spectrum reflects the pseudoaxial symmetry in the chemical shielding due to the anisotropic rotation. In order to see the full nonaveraged tensor it would be necessary to slow the reorientation down to a rate much below the shielding anisotropy. For benzene this would occur at temperatures less than about $-213^{\circ}C$.

From the spectrum in Figure 10, the principal components of the shielding tensor for benzene at $-50^{\circ}C$ are $\sigma_{\perp} = + 1.8 \pm 1.0$ ppm and $\sigma_{\parallel} = -3.5 \pm 1.0$ ppm, with the isotropic shift relative to liquid benzene being 0.0 ± 1.0 ppm. Residual broadening was 90 Hz. The anisotropy is -5.3 ± 0.3 ppm, where $\sigma_{\parallel}$ is now the least shielded component. $\Delta\sigma$ was also measured at $-100^{\circ}C$ and $-188^{\circ}C$ and found to be -5.3 ± 0.3 ppm. This value can be compared with those obtained by partial orientation of benzene in a nematic solvent, remembering that that method is less accurate than the one used in this work. The value of the

Figure 10. 1H powder spectrum of $C_6H_6(s)$ at $-50^\circ C$ relative to liquid benzene

proton shielding anisotropy reported in those studies was -2.93 ± 0.2 ppm (54) and -3.45 ± 0.7 ppm (55). Also, a theoretical value for $\Delta\sigma$ of -4.4 ppm has been reported (56), from a consideration of ring current contributions to the shielding. Finally, by way of a last comparison, in the only other study of aromatic protons (57), ferrocene also exhibited a motionally averaged axially symmetric shielding tensor, with $\Delta\sigma = -6.5 \pm 0.1$ ppm.

V. SUMMARY AND CONCLUSIONS

The proton NMR in powdered samples of $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, and $\text{C}_6\text{H}_6(\text{s})$ have been studied by multiple pulse line narrowing techniques. The resultant spectra provide nuclear magnetic shielding tensors that are (at least approximately) axially symmetric. The total anisotropy, $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ is 34.2 ± 1.0 ppm for ice, 11.1 ± 1.0 ppm for the highest-temperature phase of solid hydrogen sulfide, and -5.3 ± 0.3 ppm for benzene in the rotator phase. These values represent a new physical index of the geometry and chemical bonding in the materials studied, and, in that sense, represent the starting point for further investigations into processes which involve the electronic structure of these molecules; e.g., surface adsorption. In addition, because shielding anisotropies are derivable from molecular electronic wavefunctions, it is expected that these measured anisotropies will be of great value in assessing the quality of molecular wavefunctions.

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VIII. APPENDIX

This section contains the listings of the Fortran computer program, written by Dr. R. C. Wilson, that was used to determine the principal components of the chemical shift tensors. The program simulates an axially symmetric NMR powder pattern convoluted with a Lorentzian broadening function.

```

$JOB RYAN,TIME=45,PAGES=60
PROGRAM TO SIMULATE NMR POWDER PATTERN

INPUT FORMAT

CARD 1:(3F10.4,15,5A4)

COLUMNS 1-10:CPL-THE PARALLEL COMPONENT OF THE CHEMICAL SHIFT
TENSOR IN PPM FROM THE STANDARD
11-20:CPR-THE PERPENDICULAR COMPONENT OF THE CHEMICAL
SHIFT TENSOR IN PPM
21-30:XF-THE FREQUENCY IN MHZ
31-35:NUM-THE NUMBER OF POINTS IN THE SPECTRUM(<500)
36-55:LABEL-IDENTIFICATION TO BE PRINTED AND PLOTTED
56-60:ANY NUMBER OTHER THAN ZERO IF USING CARD 3

CARD 2:(15,7F10.4)

COLUMNS 1- 5:NZ-NUMBER OF POINTS TO BE USED TO PERFORM THE
INTEGRATION, MUST BE ODD
6-15:DZ-SIZE OF THE INTERVAL OF THE INTEGRATION, MAY
RANGE FROM 0 TO 1.0, FOR NZ=201, DZ=.005
16-25:XOFF-THE CHANNEL NUMBER CORRESPONDING TO THE STANDARD
26-35:SCF-THE FACTOR BY WHICH THE PULSE SEQUENCE SCALES THE
CHEMICAL SHIFT, FOR REV-8, SCF=2.1213
36-45:HPC-THE NUMBER OF HERTZ PER CHANNEL
46-55:XLW-THE LINEWIDTH IN HERTZ/56
56-65:ZERO-THE BASELINE OF THE EXPERIMENTAL DATA
66-75:SIZE-THE MAXIMUM HEIGHT OF THE EXPERIMENTAL DATA
ABOVE THE BASELINE

CARD 3:(3F10.4)

TO ADD A LORENTZIAN LINE TO AX SYM SHIFT
IF NO LORENTZIAN LINE-NC CARD 3

COLUMNS 1-10:XLORW-LINEWIDTH (HZ) (1/T2=2DELTA F)
11-20:PLGR-POSITION OF MAXIMUM (PPM FROM STANDARD)
21-30:FRACL-FRACTION OF INTENSITY AT MAXIMUM

CARDS 4-? (10F5.0)

THE EXPERIMENTAL DATA (HEIGHT ONLY), MUST START AT CHANNEL 1
AND END AT CHANNEL NUM.

CARDS START AGAIN AT CARD1 TO PROCESS FURTHER DATA. A BLANK CARD
(IE. NUM=0) TERMINATES THE PROGRAM

```

```

1      C      REAL DATA(500),DATAY(500),SUM(500),CC(500),X(4),Y(4),LABEL(5)
2      XLCPW=1.
3      PLCP=1.
4      WRITE (6,106)
5      READ (5,100) CPL,CPR,XF,NUM,(LABEL(I),I=1,5),FLAG
6      5 READ (5,101) NZ,DZ,XOFF,SCF,HPC,XLW,ZERO,SIZE
7      WRITE (6,102) (LABEL(I),I=1,5),CPL,CPR
8      WRITE (6,103) XLW,SCF,HPC
9      IF (FLAG.EQ.0) GOTO 6
10     READ (5,100) XLORW,PLCP,FRACL
11     WRITE (6,107) XLORW,PLCP
12     XLORW=XLORW*XF/(SCF*HPC)
13     PLCP=XOFF+PLCP*XF/(SCF*HPC)
14     GOTO 7
15     6 FRACL=0.

      C
      C      SET UP CONSTANTS
      C
16     7 SSQ=0.

      C
      C      PHASE RAISES OR LOWERS RIGHT SIDE OF SPECTRUM
      C
17     PHASE=0
18     CPL=XOFF+CPL*XF/(SCF*HPC)
19     CPR=XOFF+CPR*XF/(SCF*HPC)
20     XLW=XLW*XF/(SCF*HPC)
21     XLW2=XLW*XLW
22     CPL2=CPL*CPL
23     CPR2=CPR*CPR
24     DCS=CPL-CPR
25     CISO=(CPL+2.*CPR)/3.
26     DI=0.

      C
      C      SET UP ANGULAR FUNCTIONS
      C
27     DO 10 I=1,NZ
28     Z=DI*DZ
29     ZS=Z*Z
30     CC(I)=CPR+DCS*ZS
31     DI=I
32     10 CONTINUE

      C
      C      STEP THROUGH FREQUENCIES
      C

```

4

```

33      CCN=6.
34      TEMP=4.
35      M=NZ-1
36      DO 20 I=1,NUM
37      Z=I
38      S=XLW2/((((CC(1)-Z)**2)+XLW2)
      C
      C      INTEGRATION BY SIMPSON'S RULE INTEGRATION OVER NZ EQUAL INTERVALS
      C
39      DO 30 J=2,M
40      S=S+TEMP*XLW2/((((CC(J)-Z)**2)+XLW2)
41      TEMP=CCN-TEMP
42      30 CONTINUE
43      SUM(I)=(S+XLW2/((((CC(NZ)-Z)**2)+XLW2))*DZ/3.
44      SUM(I)=SUM(I)+286.34652*FRACL/(XLORW+((((PLOR-Z)**2)/XLORW))
45      DATAX(I)=I
46      20 CONTINUE
      C
      C      READ THE EXPERIMENTAL DATA
      C
47      READ (5,104)(DATAY(I),I=1,NUM)
      C
      C      SCALE THE COMPUTED SPECTRUM
      C
      C      FIND MAXIMUM AND MINIMUM PCINTS
      C
48      YMAX=SUM(I)
49      YMIN=SUM(I)
50      DO 40 I=2,NUM
51      IF (YMAX.LT.SUM(I))YMAX=SUM(I)
52      IF (YMIN.GT.SUM(I))YMIN=SUM(I)
53      40 CONTINUE
54      YDIF=YMAX-YMIN
      C
      C      DO THE SCALING
      C
55      DO 50 I=1,NUM
56      SUM(I)=(SUM(I)-YMIN)*SIZE/YDIF+ZERO+PHASE*I
57      SSC=SSQ+(SUM(I)-DATAY(I))**2
58      50 CONTINUE
59      SSC=SSQ/NUM
60      WRITE(6,105) SSC
61      WRITE (6,106)
      C
      C      GRAPH THE SPECTRA
      C
      C      THE COMPUTED SPECTRUM AS A SOLID CURVE

```


15-T-783

The chemical shift anisotropies of ^1H in
 $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, and $\text{C}_6\text{H}_6(\text{s})$

by

Larry Michael Ryan

A Thesis Submitted to the
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I. INTRODUCTION

The effect of the electronic environment of a nucleus upon its magnetic resonance frequency, first discovered in 1950 by Proctor and Yu (1), can be described by a symmetric, second-rank tensor, $\bar{\bar{\sigma}}$. The usefulness of this quantity is in its sensitivity to the anisotropy of the electronic environment around a nucleus. That is, the chemical shift is directly related to molecular structure (2). In conventional high resolution NMR measurements on liquids, because of rapid molecular reorientation, only the isotropic part of $\bar{\bar{\sigma}}$ is accessible, or

$$\bar{\sigma} = \frac{1}{3}\text{Tr}(\bar{\bar{\sigma}}) = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad . \quad (1)$$

The σ_{ii} are the principal components of $\bar{\bar{\sigma}}$. While the utility of this parameter is beyond contention, considerably more information is available from a knowledge of the individual quantities that characterize $\bar{\bar{\sigma}}$ (3, 4).

In order to gain experimental access to the principal components of $\bar{\bar{\sigma}}$, one requires a state, unlike the liquid, in which random motion takes place in a time scale long compared to that of the NMR experiment. One example of such a state is the solid state. However, the NMR spectra of solids are typically broad due to internuclear dipole-dipole interactions (which are averaged to zero in liquids), and again

the full chemical shift information is hidden.

For a few nuclei, such as ^{31}P , the large chemical shifts and small dipolar broadening do permit the solid state spectra to be analyzed without using special methods (5). It is only with the development of multiple pulse NMR techniques (6-8) to suppress dipolar broadening that it has become possible to determine chemical shift anisotropies in solids with strong homonuclear dipolar coupling. Other methods, such as "second moment" analysis (9), and NMR of solids partially oriented in liquid crystals (10-12) have been found to be generally unreliable. Thus, using single crystals of known structure, it becomes possible to specify the full symmetric, second-rank $\bar{\sigma}$ tensor. This would involve a specification of the chemical shielding along three orthogonal directions and the angles relating this system to the molecular coordinate system. Where powder samples are employed, only the values of the three "principal components" of $\bar{\sigma}$ are obtained, their orientation relative to the molecule being lost.

Whereas multiple pulse techniques have made possible the measurement of chemical shift tensors of ^{19}F and ^{13}C in many compounds, this state of affairs has been persistently less true for ^1H . Relative to ^1H , fluorine shielding anisotropies (the difference between two particular components) are large, around 200 ppm (13), and the dipolar broadening

relatively smaller, so that resolution requirements are less severe. Nuclei such as ^{13}C , by virtue of their low isotopic abundance, require, at most, the simpler method of strong heteronuclear decoupling (14) to furnish highly resolved spectra. In detailing chemical shift anisotropies of protons in solids, however, one must contend with the strongest dipolar coupling between nuclei, and the smallest chemical shift anisotropies. Typically these are 20-60 KHz and 1.7 KHz, respectively (3), for a spectrometer operating at 56 MHz. This "serious challenge to multiple pulse techniques" was noted by Pines et al. (15) in presenting their method of isotopic dilution with ^2H , and deuterium spin decoupling as the simplest method for obtaining chemical shift information in such systems.

It is the purpose of the studies presented in this work to show that isotopic dilution (15) is not necessary to obtain chemical shift information in solids with large homonuclear dipolar coupling, and, using multiple pulse techniques, to measure the principal components of the chemical shift tensor in three systems of experimental and theoretical interest, ice, hydrogen sulfide, and benzene.

II. THEORY

A. Basic Theory

Nuclear magnetic resonance (NMR) is a technique for studying nuclear spin environments using the absorption of radio frequency energy as a probe. The method was first developed in 1946, at Harvard, by Purcell, Torrey, and Pound (16), and independently at Stanford by Bloch, Hansen, and Packard (17). Because the background and details are well-known (18, 19), only a brief review is given.

A nucleus with spin $\vec{I}$ has a magnetic moment given by

$$\vec{\mu} = \gamma \hbar \vec{I} \quad , \quad (2)$$

where γ , the gyromagnetic ratio, is a constant for a given nucleus. A magnetic moment placed in a magnetic field H_0 , directed along the z axis, will have an interaction described by the Zeeman Hamiltonian

$$\mathcal{H}_Z = - \vec{\mu} \cdot \vec{H}_0 = - \gamma \hbar \vec{I} \cdot \vec{H}_0 = - \gamma \hbar I_z H_0 \quad . \quad (3)$$

The eigenvalues of this system are

$$E = - \gamma \hbar H_0 m \quad , \quad (4)$$

where m , the magnetic quantum number, can have the values $I, I-1, \dots -I$. Thus, the energy separation between levels is

$$\Delta E = - \gamma \hbar H_0 = \hbar \omega \quad (5)$$

The selection rule for transitions between energy levels is $\Delta m = \pm 1$, and in nuclear magnetic resonance, transitions are induced between these levels by application of a radio-frequency field, H_1 , perpendicular to H_0 with a frequency

$$\omega_0 = - \gamma H_0 \quad (6)$$

called the Larmor frequency.

B. Relaxation Phenomena

It is also important to explain two characteristic times connected with NMR. Consider for a moment a collection of nuclear spins in thermal equilibrium with one another in a strong static magnetic field, H_0 . Such nuclei will be distributed among the $2I + 1$ nuclear spin energy levels according to the Boltzmann distribution. This results in a net magnetization in the direction of the applied field (again taken to be the z direction), $M_z = M_0$. Suppose this system is disturbed in such a way as to leave $M_y = M_0$ and $M_{x,z} = 0$ (as is often done in practice). The characteristic time for the exponential decay of the nuclear spin system toward thermal equilibrium within itself is called the spin-spin (or transverse) relaxation time, T_2 (18). T_1 , called the spin-lattice (or longitudinal) relaxation time,

is the characteristic time of the spin system to approach thermal equilibrium with the lattice or heat bath which is comprised of the remaining degrees of freedom (electronic, translational, etc.) (18).

C. The Chemical Shift Tensor

From Equation 6, it is seen that the resonant frequency of a particular nucleus depends on the magnetic field it experiences. For a nucleus in a molecule, the "effective field", $\vec{H}_O + \vec{H}'$, is different from the applied field due to shielding by the electrons around the nucleus. We can write

$$\vec{H}' = - \bar{\sigma} \vec{H}_O, \quad (7)$$

where $\bar{\sigma}$ is the magnetic shielding tensor. The resonant frequency, then, is

$$\vec{\omega} = - \gamma (\vec{H}_O + \vec{H}') \quad (8)$$

$$= - \gamma (\bar{I} - \bar{\sigma}) \cdot \vec{H}_O. \quad (9)$$

The Hamiltonian for the chemical shift, which is just a modification to the Zeeman interaction is

$$\mathcal{H}_\sigma = - \gamma \hbar \bar{I} \cdot \bar{\sigma} \cdot \vec{H}_O. \quad (10)$$

The shielding tensor defined by Equation 7 is a tensor with nine components,

$$\sigma_{ij} = \begin{vmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{yz} & \sigma_{zz} \end{vmatrix}, \quad (11)$$

so that, e.g.,

$$H'_x = (\sigma_{xx}H_x + \sigma_{xy}H_y + \sigma_{xz}H_z), \quad (12)$$

etc. Because $\bar{\sigma}$ is symmetric ($\sigma_{ij} = \sigma_{ji}$) only six of these components are, in fact, different. This tensor can be diagonalized so that it has only the three diagonal elements, σ_{xx} , σ_{yy} , and σ_{zz} different from zero. Because the electronic environment about a nucleus in a molecule is generally anisotropic, these "principal components" are usually not all equal. This is given explicitly in Ramsey equation (20), which provides the basis for theoretical calculations of chemical shift tensors:

$$\begin{aligned} \sigma_{zz} = & \frac{e^2}{2mc^2} \langle 0 | \sum_i \frac{(x_i^2 + y_i^2)}{r_i^3} | 0 \rangle \\ & - \frac{e^2 \hbar^2}{2m^2 c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} [(\langle 0 | \sum_i L_{zi} | n \rangle) (\langle n | \sum_i \frac{L_{zi}}{r_i^3} | 0 \rangle)] \end{aligned}$$

$$+ (\langle 0 | \sum_i \frac{L_{zi}}{r_i^3} | n \rangle) (\langle n | \sum_i L_{zi} | 0 \rangle)] \quad (13)$$

with similar expressions for the xx and yy components. e and m are the electron charge and mass, c is the speed of light, $\langle 0 |$ indicates the ground state wave function, the sum over i is over all electrons, the sum over n is over all excited states, L_{zi} is the orbital angular momentum operator of the i^{th} electron in the z direction, the origin of the x , y , and z axes is at the nucleus in question, and r_i is the distance from the nucleus to electron i . As seen above, Ramsey separated the chemical shift tensor into two terms. The first term is positive and is known as the diamagnetic contribution to $\bar{\sigma}$. The second term is of opposite sign and is called the paramagnetic contribution.

The diamagnetic term involves only ground state wave functions, whereas the paramagnetic term involves a summation over all excited states. Thus, an exact calculation of $\bar{\sigma}$ from Equation 13 is not possible, as knowledge of the excited state wave functions is normally not available. Approximate methods of estimating the paramagnetic term have been developed (21-24) and a great number of ab initio approaches (25-27) exist, but the evaluation of Ramsey's formula remains a difficult problem.

1. Powder spectrum lineshapes

Experimental methods for determining shielding anisotropies were mentioned briefly in Chapter I. In this work, only studies of powdered solids were attempted, so only the principal elements of $\bar{\sigma}$ could be measured. This is because with powders there is a random distribution of orientations of the crystalline axes, and the resultant lineshape is a sum of the individual contributions (4, 28).

Figure 1 shows the theoretical powder spectrum lineshape for the general case where $\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$. In the case of axial symmetry, where two of the components are equal, the lineshape appears as in Figure 2. The principal shielding components can be obtained from an experimental powder spectrum by fitting it with a theoretical pattern convoluted with a broadening function (Gaussian or Lorentzian) to account for residual broadening. A computer program to do this for the axially symmetric case is given in the Appendix.

D. Multiple Pulse NMR Techniques

There are basically two ways that nuclear magnetic resonance can be observed in bulk materials (29); the continuous wave method or the pulse method. In the conventional pulse method the spin system is subjected to a short intense burst, or "pulse", of rf power that rotates the

Figure 1. The theoretical powder line shape for an arbitrary chemical shift tensor. The full curve gives the experimental line shape where residual broadening is superimposed

Figure 2. The theoretical and experimental line shapes for an axially symmetric chemical shift tensor

magnetization away from its equilibrium position. Then, while M_z relaxes back to M_0 , the transverse components make up a rotating magnetic moment which induces a signal in a detector. The observed signal, $A(t)$ vs t , called a free induction decay (FID), is the inverse Fourier transform of the cw spectrum, $A(\omega)$ vs ω (18, 30), so that the same information is contained in either representation.

In solids, as mentioned before, the NMR spectra are dominated by dipolar interactions, so that neither the continuous wave nor single pulse experiments yield much information about smaller, more chemically interesting interactions such as chemical shifts. However, with recent developments in multiple pulse experiments (6-8) it has been shown that the application of cyclic trains of rf pulses are capable of altering spin interactions so that the dipolar broadening can be selectively removed, revealing the hidden structure. Thus, the Fourier transform of these multiple pulse experiments is the conventional frequency spectrum that would be obtained from a system in which the dipolar broadening had been removed and the chemical shifts had been scaled by some measurable constant.

1. Average Hamiltonian Theory

The basic theory underlying multiple pulse NMR experiments, called Average Hamiltonian Theory, has been developed

by Waugh and others (6, 31-36). The starting point is a description of the nuclear spin system in terms of the density matrix, ρ (19). In a pulse experiment, the signal detected is proportional to a component of the nuclear spin angular momentum operator, $\vec{I}$, in the xy plane (37), or

$$\langle I_x(t) \rangle = \text{Tr}(\rho(t) I_x) \quad . \quad (14)$$

Thus, if the spin system is subjected to a train of rf pulses, the time development of the spin system is describable in terms of the time evolution of the density matrix. The equation of motion for the evolution of the density matrix is (31)

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] \quad , \quad (15)$$

where $\mathcal{H}$ is the spin Hamiltonian. In the interaction frame of the Zeeman interaction (i.e., the rotating frame) $\mathcal{H}$ can be written as

$$\mathcal{H}(t) = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{rf}}(t) \quad (16)$$

where

$$\mathcal{H}_{\text{int}} = \mathcal{H}_0 + \mathcal{H}_\sigma + \mathcal{H}_D^{(z)} \quad . \quad (17)$$

$\mathcal{H}_0$ is the offset Hamiltonian, $\mathcal{H}_\sigma$ the chemical shift, and $\mathcal{H}_D^{(z)}$ the truncated dipolar interaction; in frequency units, we have

$$\mathcal{H}_0 = -\gamma(\omega_0 - \omega)I_z \quad (18)$$

$$\mathcal{H}_\sigma = -\omega_0 \sum_i \sigma_{zzi} I_{zi} \quad (19)$$

$$\mathcal{H}_D^{(z)} = \sum_{i < j} \sum b_{ij}(\vec{r}_{ij})(\vec{I}_i \cdot \vec{I}_j - 3I_{iz}I_{jz}) \quad (20)$$

where i and j refer to the individual spins, and ω_0 is the Larmor frequency defined by Equation 6. $\mathcal{H}_{rf}$ is the Hamiltonian for the interaction between the nuclear spin system and the pulse train, and so, depends on the particular pulse sequence used.

It can be shown (31, 38) that the solution of Equation 15 may be written in terms of the density matrix $\rho(0)$, at some initial time $t = 0$, as:

$$\rho(t) = U(t,0)\rho(0)U^\dagger(t,0) \quad (21)$$

where

$$U(t,0) = U_{rf}(t,0)U_{int}(t,0) \quad (22)$$

with

$$U_{rf}(t,0) = T \exp\left[-i \int_0^t \mathcal{H}_{rf}(t')dt'\right] \quad (23)$$

and

$$U_{int}(t,0) = T \exp\left[-i \int_0^t \tilde{\mathcal{H}}_{int}(t')dt'\right] \quad (24)$$

and

$$\tilde{\chi}_{\text{int}}(t) = U_{\text{rf}}^{\dagger}(t,0) \chi_{\text{int}} U_{\text{rf}}(t,0) \quad . \quad (25)$$

T is the Dyson time ordering operator, meaning that Equations 23 and 24 are extremely complicated for an arbitrary $\chi_{\text{rf}}(t)$. However, simplifications occur by using a pulse sequence which is both periodic and cyclic, i.e.

$$\chi_{\text{rf}}(t + Nt_c) = \chi_{\text{rf}}(t) \quad (\text{periodic}) \quad (26)$$

$$\int_0^{Nt_c} \chi_{\text{rf}}(t) dt = 0 \quad , \quad (\text{cyclic}) \quad (27)$$

and by restricting observation of the spin system to integral multiples of the cycle time, t_c (35). From Equations 23 and 27,

$$U_{\text{rf}}(Nt_c, 0) = T \exp(0) = 1 \quad , \quad (28)$$

and then

$$U_{\text{int}}(Nt_c, 0) = [U_{\text{int}}(t_c, 0)]^N \quad . \quad (29)$$

Now $U(Nt_c, 0)$ can be expanded using the Magnus formula (39),

$$U_{\text{int}}(Nt_c, 0) = \exp[-iNt_c (\bar{H}_{\text{int}}^{(0)} + \bar{H}_{\text{int}}^{(1)} + \bar{H}_{\text{int}}^{(2)} + \dots)] \quad , \quad (30)$$

where

$$\bar{H}_{\text{int}}^{(0)} = \frac{1}{t_c} \int_0^{t_c} \tilde{H}_{\text{int}}(t') dt' \quad (31)$$

$$\bar{H}_{\text{int}}^{(1)} = \frac{-i}{2t_c} \int_0^{t_c} dt'' \int_0^{t''} dt' [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')] \quad (32)$$

$$\bar{H}_{\text{int}}^{(2)} = \frac{1}{6t_c} \int_0^{t_c} dt''' \int_0^{t'''} dt'' \int_0^{t''} dt' \{ [\tilde{H}_{\text{int}}(t'''), [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')]] + [\tilde{H}_{\text{int}}(t'''), [\tilde{H}_{\text{int}}(t'), [\tilde{H}_{\text{int}}(t''), \tilde{H}_{\text{int}}(t')]]] \} \quad (33)$$

The strong condition for convergence at this series is

$$t_c \|\tilde{H}_{\text{int}}(t)\| \ll 1 \quad (34)$$

At times $t = Nt_c$, then, the density matrix behaves as if it develops under an "effective" Hamiltonian

$$\bar{H}_{\text{int}} = \bar{H}_{\text{int}}^{(0)} + \bar{H}_{\text{int}}^{(1)} + \bar{H}_{\text{int}}^{(2)} + \dots \quad (35)$$

which is time independent. By our choice for χ_{rf} , we can thus control the Hamiltonian under which the spin system appears to evolve, and obtain results which are quite

different from conventional NMR experiments. In the limit of short t_c , the higher order correction terms vanish, and this Hamiltonian just becomes $\bar{H}_{int}^{(0)}$, called the "average" Hamiltonian.

2. The eight pulse cycle

Most applications of the theory outlined above have been in the development of pulse sequences which will remove or attenuate the dipolar broadening in solids (6-8). One such sequence is the REV-8 pulse cycle (8) shown in Figure 3. The average Hamiltonian for the eight pulse cycle, assuming an $\mathcal{H}_{int}$ given by Equation 17, is (40)

$$\bar{\mathcal{H}}_{\Delta\omega}^{(0)} = \frac{1}{3} \sum_i (\Delta\omega) [(1+2a)(I_{xi} + I_{zi}) - \epsilon_i I_{zi}] \quad (36)$$

$$\bar{\mathcal{H}}_{\sigma}^{(0)} = \frac{1}{3} \sum_i (\omega_{\sigma} \sigma_{zzi}) [(1+2a)(I_{xi} + I_{zi}) - \epsilon_i I_{zi}] \quad (37)$$

$$\bar{\mathcal{H}}_D^{(0)} = 0 \quad (38)$$

$$a = \frac{3t_w}{t_c} \left(\frac{4}{\pi} - 1 \right), \quad (39)$$

where the effect of finite pulse length error, ϵ_i , and finite pulse width, t_w , have been taken into account. As can be seen, the average Hamiltonian has no contribution from the dipolar Hamiltonian to first order. The effective

Figure 3. REV-8 pulse cycle

field is pointing along the $[101]$ direction, and so the chemical shift and resonance offset will be scaled by $\sqrt{2} (1+2a)/3$. In Figure 3, P_x refers to a rotation of the magnetization by 90° about the x axis in the rotating frame, and $\tau = t_c/12$.

III. EXPERIMENTAL METHODS

A. The Equipment

The pulse NMR spectrometer used in these experiments was similar to those of Ellett et al. (41) and Vaughan et al. (42), and has been described elsewhere (43). The block diagram is shown in Figure 4. It is a single sideband unit capable of broadband operation, operating at a frequency of 56.5 MHz for protons. A deuterium lock stabilized the spectrometer to within 10 Hz to permit signal averaging. The pulse programmer allowed for the utilization of any sequence of up to 24 pulses in four channels, differing by an adjustable rf phase. The transmitter was an IFI model 404 distributed amplifier system, capable of 500 watts in pulsed operation. With proper matching of transmitter to probe, and a probe Q of 45, $\pi/2$ pulses could be generated in 1.25 microseconds. Total dead time between turn off of pulse entering the power amplifier and reception of undistorted NMR signal was 1.5 microseconds, of which all but 10 nanoseconds was associated with probe ring-down. Briefly, the receiver consisted of three stages, the first two being Spectrum Microwave Model SMLD-10 limiting amplifiers, and the third being an Avantek Model UTO-50L amplifier. The unit was tuned to the operating frequency by inserting series tuned LC circuits between the first and second, and second and third stages. The transient recorder was a

Figure 4. Schematic of the pulsed nuclear magnetic resonance equipment

Biomation 805, with minimum sampling time of 0.2 microseconds per channel. The memory of the unit contains 2048 eight bit words. The Biomation is interfaced to a PDP 11/10 computer for signal averaging and data manipulation.

The homogeneity of the H_1 field is indicated by the decay (8) in Figure 5, taken on a sample of water. The figure exhibits the response to $128 \pi/2$ pulses over a time scan of 100 msec.

B. Experimental Procedure

The pulse sequence used was the REV-8 pulse sequence (8) which removes homonuclear dipolar interactions to second order and minimizes experimental artifacts relative to the WAHUHA 4-pulse cycle (6). The tuning procedure for multiple pulse experiments has been given in detail elsewhere (42) and will not be repeated. Spectra of both ice and solid H_2S were measured relative to liquid water at room temperature. The temperature of the solids was -100°C , controlled to within $\pm 2^\circ\text{C}$ with a Varian V-4343 NMR Variable Temperature Controller. Temperature was measured with a chromel-alumel thermocouple. Spectra of solid benzene were obtained at -50°C , -100°C , and -188°C , referenced to the liquid at room temperature. Solid hydrogen sulfide was prepared from commercial gas by condensation in an evacuated tube submerged in liquid nitrogen. This tube was then transferred to the

Figure 5. The response of protons to 128 $\pi/2$ pulses. The total scan shown is 100 msec

NMR probe at -100°C . Powdered ice and benzene were obtained simply by freezing the liquid standard in the probe. In all cases the samples were contained in standard 5 mm NMR tubes and were less than 5 mm in length.

A free induction decay of ice at -100°C was characterized by a T_2^* of $9.4 \mu\text{sec}$, and is shown in Figure 6. T_2^* is the transverse relaxation time plus an instrumental contribution due to magnetic field inhomogeneity. The strong convergence criterion for choosing a multiple pulse cycle time which will average a given interaction is

$$t_c = \|\tilde{H}_{\text{int}}(t)\| \ll 1 \quad . \quad (34)$$

$\|\tilde{H}_{\text{int}}(t)\|$ is the magnitude of the internal interaction in the frame of the rf signal. Thus, if

$$\|\tilde{H}_{\text{int}}(t)\| \approx (\pi T_2^*)^{-1} \quad , \quad (40)$$

the criterion for multiple pulse narrowing of the proton spectrum in ice is $t_c \ll 30 \mu\text{sec}$. A value of $t_c = 27.6 \mu\text{sec}$ was found to be sufficiently short for removal of dipolar broadening in $\text{H}_2\text{O}(\text{s})$ and also in $\text{H}_2\text{S}(\text{s})$ and $\text{C}_6\text{H}_6(\text{s})$.

T_1 for the highest-temperature phase of solid H_2S is known to be quite short (44), and the 10 seconds allowed for spin-lattice recovery was more than enough to accommodate the usual $5 T_1$ (37). Ice, on the other hand, has a long T_1

Figure 6. A free induction decay of ice at -100°C . The total scan shown is $100\ \mu\text{sec}$

(45), and it is doubtful if this condition was ever satisfied in this system. In varying the sampling rate from 300 to 1000 seconds, however, no change was observed in the decay or subsequent Fourier transform frequency spectrum. In benzene at -50°C and -100°C , T_1 is again short (46) and the sampling time was 15 sec. At -188°C , however, T_1 increases to about 1000 seconds (46). The procedure used in this case was to melt the sample between scans and allow the magnetization to reach equilibrium in this state (where T_1 was much shorter) before refreezing.

At the beginning of each experiment, calibration markers spaced 1KHz apart were generated using a liquid sample, as illustrated by Figure 7. These markers allowed a determination of the chemical shift scaling factor (8). The value of the scaling factor in the present experiments may be estimated by a consideration of the average Hamiltonian under the REV-8 sequence, taking into account only finite pulse widths.

$$\bar{H} = \frac{1}{3} \sigma \left[1 + \frac{6t_w}{t_c} \left(\frac{4}{\pi} - 1 \right) \right] [I_z + I_x] \quad (41)$$

where t_w is the pulse length for a $\pi/2$ pulse. Ignoring phase transient effects and H_1 inhomogeneities, then, the scaling factor is

Figure 7. Liquid chemical shift markers spaced 1 KH_2 apart

$$S = \frac{\sqrt{2}}{3} \left[1 + \frac{6t_w}{t_c} \left(\frac{4}{\pi} - 1 \right) \right] . \quad (42)$$

The pulse width in the present experiments was 1.25 μ sec, so that the anticipated reciprocal of the scaling factor, for a cycle time of 27.6 μ sec, is 1.98. In the present measurements, the experimental scaling factor was determined to be 1.98 ± 0.03 .

IV. RESULTS AND DISCUSSION

A. $\text{H}_2\text{O}(\text{s})$

Figure 8 shows the powder spectrum of ^1H in ice. The crosses are experimental points. The solid curve is a computer fit for an axially symmetric chemical shift tensor convoluted by a Lorentzian broadening function (47), 280 Hz in width. It is seen that the shielding is approximately axially symmetric, as is the general case for protons in hydrogen bonds (3, 4). The principal values furnished by a statistical best fit of the theoretical line are $\sigma_{\perp} = -6.5 \pm 0.6$ ppm and $\sigma_{\parallel} = +27.7 \pm 1.0$ ppm relative to liquid water. There is a ± 0.3 ppm uncertainty in the placement of the reference shift, so that the indicated chemical shift anisotropy ($\sigma_{\parallel} - \sigma_{\perp}$) is 34.2 ± 1.0 ppm. There is an isotropic shift of 4.8 ± 0.7 ppm from liquid water. This value for the overall anisotropy compares favorably with the value of 34 ± 4 ppm obtained in reference 15. The principal values and the isotropic shift are, however, significantly different. Unfortunately, the authors did not say what bulk susceptibility corrections were or were not made, so it is not possible to make absolute comparisons with the present data.

Theoretical studies of the magnetic shielding in protons hydrogen bonded to oxygen are also available (48, 49). In these studies, the unique axis of the σ tensor is found

Figure 8. Multiple pulse NMR powder spectrum of ^1H in $\text{H}_2\text{O}(\text{s})$ at -100°C relative to liquid water

to be parallel to the hydrogen bond, a result also characteristic of single crystal studies (3). For an H-O.....H separation of 2.76 Å, as in ice (50), the recently published ab initio calculation by Ditchfield (48) suggests that the anisotropy in the chemical shift tensor should be about 33 ppm. Lau and Vaughan (49), using a different approach, separate the chemical shift tensor into "geometrical" and "chemical" contributions, where "geometrical" refers to the relative positions of the nuclei in a molecule, and "chemical" to the electronic interactions associated with chemical bonding. For an O-H.....O separation of 2.7 Å, these authors plot the purely geometrical contribution to the anisotropy in the chemical shift vs. the O-H bond distance. For ice, in which the O-H separation is 1.01 Å (50), their model predicts this contribution to be roughly 33 ppm. Thus, the present data suggest that the tensor is determined almost entirely by the geometry of the hydrogen bond.

B. H₂S(s)

The proton spectrum of hydrogen sulfide at 173 K is shown in Figure 9. Hydrogen sulfide at atmospheric pressure solidifies at -85.6°C and undergoes phase transitions at -147.0°C and 169.7°C. Whereas there is some evidence for hydrogen bonding in the low-temperature tetragonal phase

Figure 9. ¹H powder spectrum of H₂S(s) at -100°C relative to liquid water

(51), the higher-temperature phases are generally thought to be molecular solids in which the molecules are bound together by van der Waals' forces (44, 51). The Lorentzian broadening function used to fit the spectrum in Figure 9 was 350 Hz wide. The principal values obtained were $\sigma_{\perp} = -10.0 \pm 0.8$ ppm and $\sigma_{\parallel} = +1.1 \pm 0.8$ ppm relative to room temperature water. Again, a portion of the uncertainty is in the reference sample, and so, the total anisotropy in the chemical shift is 11.1 ± 1.0 ppm. It was not found necessary to correct the values for bulk susceptibility effects.

This is the first determination of the chemical shift tensor of a hydrogen bonded to sulfur. No theoretical calculations exist for the chemical shielding in H_2S . It is not possible at this time, then, to draw conclusions about the nature of the bonding in $\text{H}_2\text{S(s)}$ from this measurement. Data on hydroxyl protons have shown the anisotropy in the shielding tensor to be much larger in the hydrogen bonded case than in the nohydrogen bonded case. Further studies of chemical shielding tensors in S-H bonded systems, including species where hydrogen bonding to sulfur is thought to exist (52), may hopefully reveal a similar correlative relationship.

C. $C_6H_6(s)$

At temperatures above $-188^{\circ}C$, benzene molecules are known to rotate rapidly about their six-fold axes (46, 53). This motion results in the components of the shielding tensor perpendicular to the rotation axis being averaged, forcing the shielding tensor to be axially symmetric. This is seen in Figure 10, which shows the powder spectrum of 1H in C_6H_6 at $-50^{\circ}C$. The spectrum reflects the pseudoaxial symmetry in the chemical shielding due to the anisotropic rotation. In order to see the full nonaveraged tensor it would be necessary to slow the reorientation down to a rate much below the shielding anisotropy. For benzene this would occur at temperatures less than about $-213^{\circ}C$.

From the spectrum in Figure 10, the principal components of the shielding tensor for benzene at $-50^{\circ}C$ are $\sigma_{\perp} = +1.8 \pm 1.0$ ppm and $\sigma_{\parallel} = -3.5 \pm 1.0$ ppm, with the isotropic shift relative to liquid benzene being 0.0 ± 1.0 ppm. Residual broadening was 90 Hz. The anisotropy is -5.3 ± 0.3 ppm, where $\sigma_{\parallel}$ is now the least shielded component. $\Delta\sigma$ was also measured at $-100^{\circ}C$ and $-188^{\circ}C$ and found to be -5.3 ± 0.3 ppm. This value can be compared with those obtained by partial orientation of benzene in a nematic solvent, remembering that that method is less accurate than the one used in this work. The value of the

Figure 10. ^1H powder spectrum of $\text{C}_6\text{H}_6(\text{s})$ at -50°C relative to liquid benzene

proton shielding anisotropy reported in those studies was -2.93 ± 0.2 ppm (54) and -3.45 ± 0.7 ppm (55). Also, a theoretical value for $\Delta\sigma$ of -4.4 ppm has been reported (56), from a consideration of ring current contributions to the shielding. Finally, by way of a last comparison, in the only other study of aromatic protons (57), ferrocene also exhibited a motionally averaged axially symmetric shielding tensor, with $\Delta\sigma = -6.5 \pm 0.1$ ppm.

V. SUMMARY AND CONCLUSIONS

The proton NMR in powdered samples of $\text{H}_2\text{O}(\text{s})$, $\text{H}_2\text{S}(\text{s})$, and $\text{C}_6\text{H}_6(\text{s})$ have been studied by multiple pulse line narrowing techniques. The resultant spectra provide nuclear magnetic shielding tensors that are (at least approximately) axially symmetric. The total anisotropy, $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ is 34.2 ± 1.0 ppm for ice, 11.1 ± 1.0 ppm for the highest-temperature phase of solid hydrogen sulfide, and -5.3 ± 0.3 ppm for benzene in the rotator phase. These values represent a new physical index of the geometry and chemical bonding in the materials studied, and, in that sense, represent the starting point for further investigations into processes which involve the electronic structure of these molecules; e.g., surface adsorption. In addition, because shielding anisotropies are derivable from molecular electronic wavefunctions, it is expected that these measured anisotropies will be of great value in assessing the quality of molecular wavefunctions.

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Dr. Richard Wilson wrote the computer program in Appendix A and assisted with some of the initial work. Rich should also be acknowledged for many helpful discussions (including some about science and even this work).

Mr. Larry Kopp laughed me about graduate school, and I wish to thank him for it here (even though I suspect it will send a shudder through some who read this).

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Finally, I would like to express my appreciation to Lynn for her patience and continued good humor.

VIII. APPENDIX

This section contains the listings of the Fortran computer program, written by Dr. R. C. Wilson, that was used to determine the principal components of the chemical shift tensors. The program simulates an axially symmetric NMR powder pattern convoluted with a Lorentzian broadening function.

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$JOB RYAN,TIME=45,PAGES=60
PROGRAM TO SIMULATE NMR POWDER PATTERN

INPUT FORMAT

CARD 1:(3F10.4,15,5A4)

COLUMNS 1-10:CPL-THE PARALLEL COMPONENT OF THE CHEMICAL SHIFT
          TENSOR IN PPM FROM THE STANDARD
          11-20:CPR-THE PERPENDICULAR COMPONENT OF THE CHEMICAL
          SHIFT TENSOR IN PPM
          21-30:XF-THE FREQUENCY IN MHZ
          31-35:NUM-THE NUMBER OF POINTS IN THE SPECTRUM(<500)
          36-55:LABEL-IDENTIFICATION TO BE PRINTED AND PLOTTED
          56-60:ANY NUMBER OTHER THAN ZERO IF USING CARD 3

CARD 2:(15,7F10.4)

COLUMNS 1- 5:NZ-NUMBER OF POINTS TO BE USED TO PERFORM THE
          INTEGRATION, MUST BE ODD
          6-15:DZ-SIZE OF THE INTERVAL OF THE INTEGRATION, MAY
          RANGE FROM .2 TO 1.0, FOR NZ=201, DZ=.005
          16-25:XOFF-THE CHANNEL NUMBER CORRESPONDING TO THE STANDARD
          26-35:SCF-THE FACTOR BY WHICH THE PULSE SEQUENCE SCALES THE
          CHEMICAL SHIFT, FOR REV-8, SCF=2.1213
          36-45:HPC-THE NUMBER OF HERTZ PER CHANNEL
          46-55:XLW-THE LINWIDTH IN HERTZ/56
          56-65:ZERO-THE BASELINE OF THE EXPERIMENTAL DATA
          66-75 SIZE-THE MAXIMUM HEIGHT OF THE EXPERIMENTAL DATA
          ABOVE THE BASELINE

CARD 3:(3F10.4)

TO ADD A LORENTZIAN LINE TO AX SYM SHIFT
IF NO LORENTZIAN LINE-NC CARD 3

COLUMNS 1-10:XLOW-LINWIDTH (HZ) (1/T2=2DELTA F)
          11-20:PLGR-POSITION OF MAXIMUM (PPM FROM STANDARD)
          21-30:FRACL-FRACTION OF INTENSITY AT MAXIMUM

CARDS 4-? (10F5.0)

THE EXPERIMENTAL DATA (HEIGHT ONLY), MUST START AT CHANNEL 1
AND END AT CHANNEL NUM.

CARDS START AGAIN AT CARD1 TO PROCESS FURTHER DATA. A BLANK CARD
(IE. NUM=0) TERMINATES THE PROGRAM

```

```

1      C      REAL DATA(500),DATAY(500),SUM(500),CC(500),X(4),Y(4),LABEL(5)
2      XLCPW=1.
3      PLCP=1.
4      WRITE (6,106)
5      READ (5,100) CPL,CPR,XF,NUM,(LABEL(I),I=1,5),FLAG
6      5 READ (5,101) NZ,DZ,XOFF,SCF,HPC,XLW,ZERO,SIZE
7      WRITE (6,102) (LABEL(I),I=1,5),CPL,CPR
8      WRITE (6,103) XLW,SCF,HPC
9      IF (FLAG.EQ.0) GOTO 6
10     READ (5,100) XLORW,PLCP,FRACL
11     WRITE (6,107) XLORW,PLCP
12     XLORW=XLORW*XF/(SCF*HPC)
13     PLCP=XOFF+PLCP*XF/(SCF*HPC)
14     GOTO 7
15     6 FRACL=0.

      C
      C      SET UP CONSTANTS
      C
16     7 SSQ=0.

      C
      C      PHASE RAISES OR LOWERS RIGHT SIDE OF SPECTRUM
      C
17     PHASE=0
18     CPL=XOFF+CPL*XF/(SCF*HPC)
19     CPR=XOFF+CPR*XF/(SCF*HPC)
20     XLW=XLW*XF/(SCF*HPC)
21     XLW2=XLW*XLW
22     CPL2=CPL*CPL
23     CPR2=CPR*CPR
24     DCS=CPL-CPR
25     CISQ=(CPL+2.*CPR)/3.
26     DI=0.

      C
      C      SET UP ANGULAR FUNCTIONS
      C
27     DO 10 I=1,NZ
28     Z=DI*DZ
29     ZS=Z*Z
30     CC(I)=CPR+DCS*ZS
31     DI=I
32     10 CONTINUE

      C
      C      STEP THROUGH FREQUENCIES
      C

```

7

```

33      CCN=6.
34      TEMP=4.
35      M=NZ-1
36      DO 20 I=1,NUM
37      Z=I
38      S=XLW2/((((CC(1)-Z)**2)+XLW2)
      C
      C      INTEGRATION BY SIMPSON'S RULE INTEGRATION OVER NZ EQUAL INTERVALS
      C
39      DO 30 J=2,M
40      S=S+TEMP*XLW2/((((CC(J)-Z)**2)+XLW2)
41      TEMP=CCN-TEMP
42      30 CONTINUE
43      SUM(I)=(S+XLW2/((((CC(NZ)-Z)**2)+XLW2))*CZ/3.
44      SUM(I)=SUM(I)+286.34652*FRAC1/(XLORW+((((PLOR-Z)**2)/XLORW))
45      DATAX(I)=I
46      20 CONTINUE
      C
      C      READ THE EXPERIMENTAL DATA
      C
47      READ (5,104)(DATAY(I),I=1,NUM)
      C
      C      SCALE THE COMPUTED SPECTRUM
      C
      C      FIND MAXIMUM AND MINIMUM PCINTS
      C
48      YMAX=SUM(1)
49      YMIN=SUM(1)
50      DO 40 I=2,NUM
51      IF (YMAX.LT.SUM(I))YMAX=SUM(I)
52      IF (YMIN.GT.SUM(I))YMIN=SUM(I)
53      40 CONTINUE
54      YDIF=YMAX-YMIN
      C
      C      DO THE SCALING
      C
55      DO 50 I=1,NUM
56      SUM(I)=(SUM(I)-YMIN)*SIZE/YDIF+ZERO+PHASE*I
57      SSC=SSQ+(SUM(I)-DATAY(I))**2
58      50 CONTINUE
59      SSC=SSQ/NUM
60      WRITE(6,105) SSC
61      WRITE(6,106)
      C
      C      GRAPH THE SPECTRA
      C
      C      THE COMPUTED SPECTRUM AS A SOLID CURVE

```

IOWA PRODUCTION TESTING LETTER

SIRE SUMMARY ISSUE

TAKE ANOTHER LOOK!

You are well aware that:

- (1) The USDA sire summaries are accurate, effective, and easily used.
- (2) A.I. associations have a wide selection of top sires for your use.
- (3) A.I. sires are greatly superior to non-AI sires in transmitting producing ability to their daughters.
- (4) In fact, our natural service sires as a group are very mediocre and are slowing the genetic improvement of herds in which they are used.

Based on this information, the best advice for a dairyman to follow in his breeding program is to select high Predicted Difference A.I. sires. Let's take another look, however, at how this is being interpreted by some within the industry. Many dairymen are still grasping for the "art" of breeding a more profitable herd of dairy cattle. These dairymen feel that they can breed a more profitable cow by paying attention to feet and legs, udder attachments and suspension, disposition, mastitis resistance, size, depth of body, dairyness, and other traits. This in itself is not wrong and some of these are important. But the net result is that many A.I. sires with PD's in the +300, +400, and +500 pound area for milk are being used because someone recommended that bull to improve the height and width of rear udder attachment, scale, or some other trait. These are still herd-improving sires for production though, aren't they? ... +300, +400, +500? Let's take another look!

Prepared by Basil R. Eastwood, Ron L. Orth and Donald E. Voelker

DyS-1986

March, 1977

Average PD values for bulls summarized in Winter 1977 by breed

	Active AI bulls				Non-AI bulls			
	Number	PDM	% Test	PDF	Number	PDM	% Test	PDF
Ayrshire	26	+464	-.02	+16	143	+35	-.00	-1
Guernsey	90	+409	-.04	+15	487	-15	+.01	0
Holstein	1,011	+480	-.05	+10	4,852	-133	-.02	-7
Jersey	122	+539	-.09	+19	509	+32	-.02	0
Brown Swiss	44	+537	-.03	+18	174	+48	.00	+2
Milking Shorthorn	10	+762	.00	+28	95	+174	.00	+6
ALL BREEDS	1,303	+484	-.05	+12	6,260	-98	-.02	-5

A very important observation was made by Bennet Cassell of USDA in regard to this situation. "While the average PDM of all bulls summarized in all breeds was +10 lb, it is important to note that a zero PDM active AI bull is not average for the AI bulls. The genetic improvement in a specific herd resulting from use of bulls of a certain PD level is a function of the genetic level of that herd. However, for most herds using AI, genetic improvement from a +500 lb AI bull would be negligible. Certainly, use of +500 lb AI bulls in the average herd would result in less than optimum genetic progress. We recommend strongly that dairymen concern themselves with differences between bulls' PD's rather than the absolute level of the PD itself."

(Some of the underlining was added to Bennet's comments.) From this, the best advice a dairyman can be given is still to select the best sires on PD from among those available. But, don't be lulled into thinking that sacrifices in PD of the sires you select won't hurt the genetic improvement for production of your herd. Be aware of how much you sacrifice in production each time you accept a lower PD in hopes of obtaining a stronger fore-udder attachment, deeper heel, or improvement in some other trait. If the possible improvement in that other trait is worth more than the potential loss in production, the sacrifice should be made. But remember that at some point in the sacrifices, you stop making genetic improvement for production with your dairy herd.

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