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NMR experiments on polycrystalline samples are discussed which allow determination of local structural information, bond angles, and bond distances, as well as furnish information to locate the principle axes of the chemical shift tensor in the molecular frame.

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STRUCTURAL INFORMATION IN POLYCRYSTALLINE SYSTEMS VIA DIPOLAR MODULATED CHEMICAL SHIFT SPECTRA*

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Abstract NMR experiments on polycrystalline samples are discussed which allow determination of local structural information, bond angles and bond distances, as well as furnish information to locate the principle axes of the chemical shift tensor in the molecular frame.

The information inherently available from a number of orientationally dependent NMR interactions is normally not obtainable in full without single crystal rotation studies. In this paper we discuss two prototype experiments which furnish a correlation between chemical shift and dipolar interactions[1,2] and, thus, allow extraction of the orientationally dependent information. The use of similar correlations has been demonstrated by Müller et al.[3], and Alla and Lippmaa[4] and has been dealt with more extensively by Hester et al.[5,6,7] and Waugh[8]. Stoll et al.[1,2] have demonstrated the production and control of such correlations with multiple pulse techniques[1], and have reported one scheme particularly useful for polycrystalline solids[2].

Our multiple pulse double resonance scheme[2] is illustrated in Fig. 1A. Briefly, one creates an S (dilute spin) transverse magnetization, allows it to evolve under the I-S heteronuclear dipolar Hamiltonian for a time, τ, while simultaneously using the multiple pulse cycle to suppress homonuclear dipolar interactions in the I (abundant spin) system, and finally, while decoupling the I spins, a π pulse on the S spin system is used to refocus the chemical shift evolution. The second half of the echo formed is Fourier transformed to produce the spectra such as those illustrated on the left half of Fig. 2. Such spectra are essentially chemical shift powder patterns for the S spins with

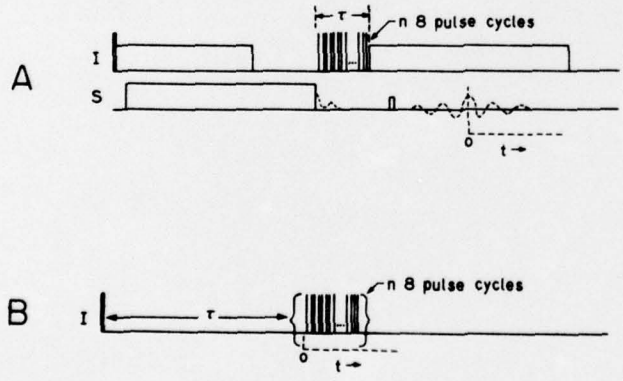

Figure 1. The pulsing sequences used in (A) the heteronuclear and (B) homonuclear experiments.

the amplitude of the various components modulated by the heteronuclear dipolar interaction[2]. Therefore, the line shapes are highly sensitive to the length of the internuclear vectors and their orientation relative to the chemical shift tensor. Spectra taken on benzene in its rotator phase near -90°C are compared with spectra synthesized[2] from the known chemical shift and geometry of benzene in Fig. 2, and one observes both qualitative and quantitative agreement. The heteronuclear dipolar interaction considered for the theoretical calculation[1] included a carbon and the six protons in the benzene molecule. In our initial paper[2] only the nearest proton was considered, and the results differed substantially for values of τ over 250 μsec.

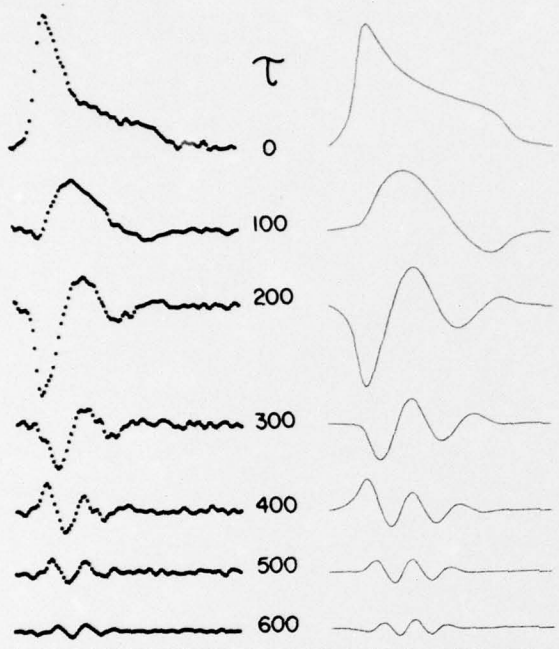

Figure 2. Calculated and experimental benzene spectra as a function of the dipolar evolution time, τ.

Another simple way of noting the influence of secondary neighbors is to consider the areas of the spectra as a function of the dipolar evolution time τ. The expression for the relative area as a function of τ is independent of the orientation of the chemical shift tensor, i.e.,

$$\frac{A(\tau)}{A(0)} = \frac{1}{4\pi} \oint \prod_i \left[\cos\left\{ \frac{\alpha\tau\, \gamma_i \gamma_j \hbar}{3\sqrt{2}\, r_{ij}} (1 - 3\cos^2\theta_{ij}) \right\} \right] d\Omega$$

where the nomenclature is the same as in reference 2. Fig. 3A illustrates such results for benzene where the dotted line represents the theoretical results considering only the nearest neighbor C-H interaction while the solid line considers all six protons within the benzene molecule.

Fig. 3B shows experimental results for the relative areas of calcium formate[2] together with two calculations using the above equation. The solid line was obtained considering only the nearest neighbor C-H interaction of the formate ion at the expected interatomic distance of 1.09 Å while the dotted line was obtained with an interatomic distance of 1.19 Å which was that required to fit the experimental area ratio at τ = 50 μsec. In general, it was not possible to account for the calcium formate areas with any static

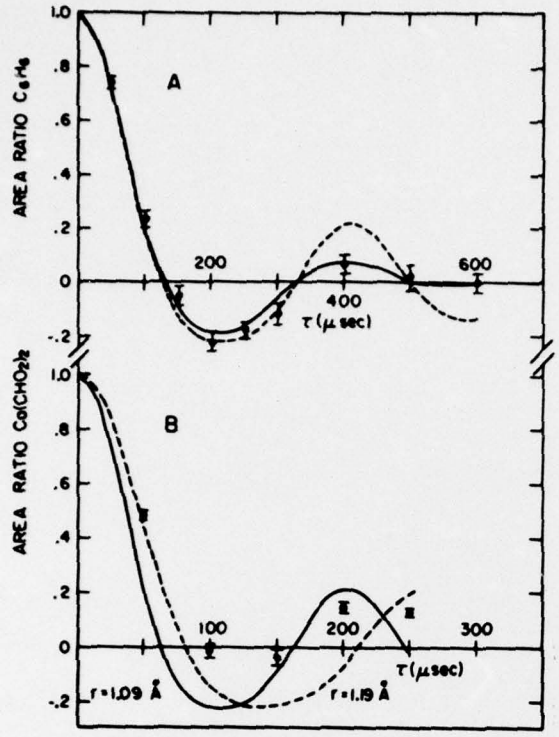

Figure 3. Comparison of calculated and experimental area ratios as a function of τ; (A) for benzene and (B) for calcium formate.

geometry (the effects of secondary neighbors is small here). Consequently it is suggested that the formate ion is not static in calcium formate but is undergoing restricted molecular motion. The heteronuclear dipolar interaction is a function of thermally averaged geometrical parameters, and efforts are presently under way to use detailed computer fits to the observed spectra in calcium formate[2] to characterize the nature of the motion present.

The pulsing scheme reproduced in Fig. 1B illustrates a means of performing a homonuclear experiment quite similar to the heteronuclear experiment discussed above. In this case it is the homonuclear dipolar interaction rather than the heteronuclear dipolar interaction which modulates the chemical shift spectra, but the experiment can be understood and analyzed in a similar fashion. That is, an initial 90° pulse produces a transverse magnetization which evolves under the influence of the homonuclear dipolar interaction for a period τ, and then a multiple pulse sequence is used to record the chemical shift powder pattern. (No refocusing pulse is used here since the proton chemical shift tensor is small, and thus some chemical shift and off resonance evolution does occur during τ. However for other nuclei a single π pulse could be placed at τ/2.) Fig. 4 shows spectra of this type for polycrystalline CCl_3COOH taken at a variety of dipolar oscillation times, τ, up to near 300 μsec. CCl_3COOH dimerizes and forms proton pairs in the solid, such that the homonuclear dipolar modulation allows the determination of the length and direction of the proton-proton vector in the chemical shift principle axes frame. Consequently, this experiment provides much information concerning the orientation of the shift tensor in the molecular frame.

These experiments are presented to illustrate how couplings between

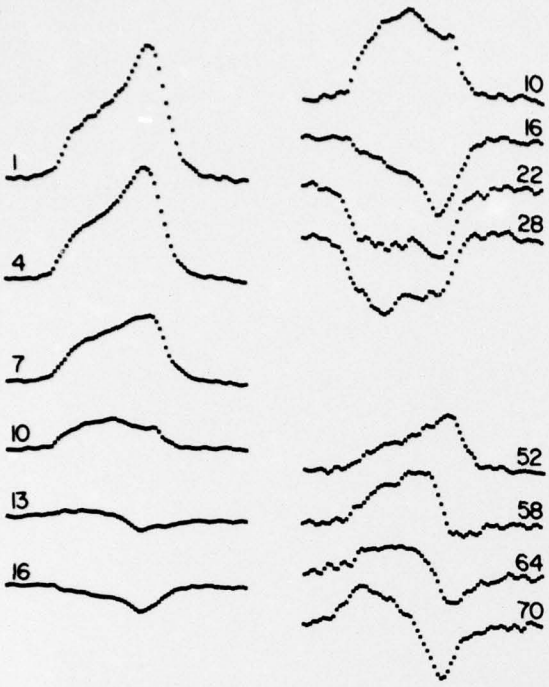

Figure 4. Experimental spectra for CCl_3COOH using the pulsing sequence illustrated in Fig. 1B. The number near each spectrum designates, when multiplied by 4.17 μsec, the dipolar evolution time, τ, i.e., τ ranged from 4.17 μsec to near 292 μsec.

orientationally dependent interactions can be designed to furnish detailed orientational information on polycrystalline samples. They represent only an initial effort on the development of what is possibly a large variety of such schemes.

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