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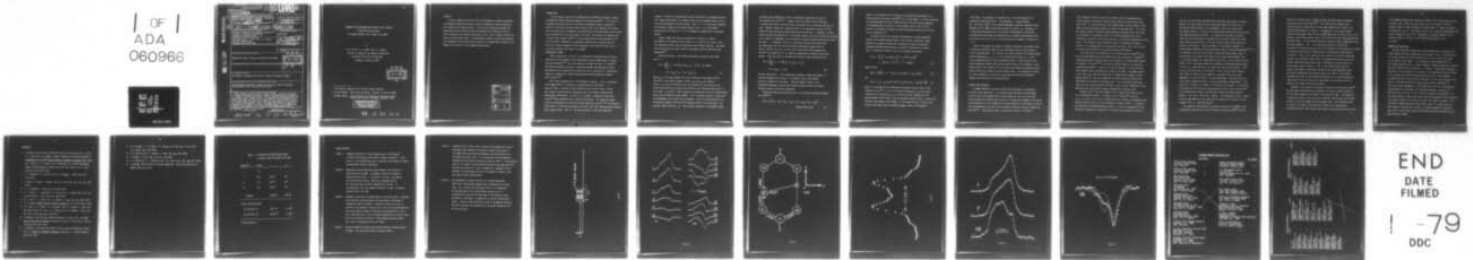
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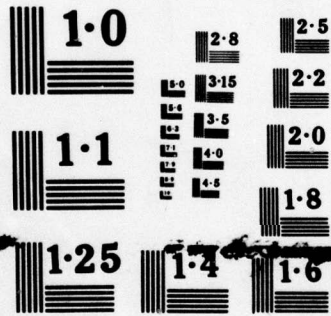
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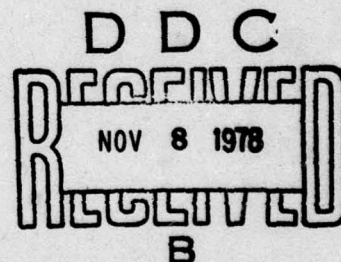
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HOMONUCLEAR DIPOLAR-MODULATED CHEMICAL SHIFT SPECTRA
IN POLYCRYSTALLINE SOLIDS:
THE PROTON CHEMICAL SHIFT TENSOR IN $\text{CCl}_3\text{COOH}^*$

by

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ABSTRACT

A single resonance, multiple pulse nuclear magnetic resonance experiment is proposed and demonstrated which produces a homonuclear dipolar modulation of a chemical shift powder pattern. The correlation generated between the homonuclear dipolar Hamiltonian and the chemical shift Hamiltonian can be used to determine the relative orientation of the chemical shift principal axis frame to the molecular frame. The experimental scheme is applied to determine the orientation of the proton-proton vector in a CCl_3COOH dimer relative to the chemical shift tensor of the hydrogen-bonded proton.

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INTRODUCTION

In this paper we describe and demonstrate an experimental scheme to produce a homonuclear dipolar-modulated chemical shift powder pattern⁽¹⁾. This type of experiment furnishes relative orientational information between internuclear vectors in the crystal and the three principal axes of the chemical shift tensor, and it has been used to determine the orientation of the proton-proton vector within the trichloroacetic acid dimer found in the solid. The results are compared with a recent single crystal study⁽²⁾, and the polycrystalline study reported here is seen to furnish information not obtainable from the single crystal study and to allow a unique assignment of the orientation of the three principal axes of the proton chemical shift tensor in CCl_3COOH .

EXPERIMENTAL SCHEME

Within recent years, the use of a correlation of the heteronuclear dipolar Hamiltonian and the chemical shift Hamiltonian has been demonstrated in several related experiments⁽³⁻⁶⁾ and, more recently, has been the topic of a review⁽⁷⁾. The present experiment produces a correlation between the homonuclear dipolar Hamiltonian and the chemical shift tensor and can be considered as a homonuclear analog of a scheme which produces heteronuclear dipolar-modulated chemical shift spectra^(1,6).

The rf pulses sequence used is illustrated in Figure 1. First, a transverse proton magnetization is created by the application of a 90° pulse. A period of time, τ , follows in which nothing is done to the I spins. During this dipolar evolution period, the proton pairs are strongly coupled by the dipole-dipole Hamiltonian. At time $t = 0$, we apply a sequence of eight-pulse cycles⁽⁸⁾ which suppresses the I-I dipolar interaction. By viewing the magnetization stroboscopically at the end of each eight-pulse cycle⁽⁸⁻¹⁰⁾, one acquires a signal which is Fourier-transformed to yield the solid state high-resolution chemical shift powder pattern. That is, during the period, t , when the eight-pulse

sequence is applied, the homonuclear dipolar Hamiltonian is suppressed and the next largest Hamiltonians, the chemical shift and off-resonance terms, control the time development of the spin system. Thus, if $\tau = 0$, the Fourier transform will produce a chemical shift powder pattern, and if $\tau \neq 0$, the dipolar evolution will be frozen at τ , $t = 0$, and appear as a modulation of the powder pattern.

Figure 2 shows such spectra collected for a series of τ values. The numbers on the spectra are the values of τ in units of $4.17 \mu\text{sec}$, so the last spectrum has had a dipolar modulation time of almost $300 \mu\text{sec}$. The eight-pulse cycle time was $50 \mu\text{sec}$, and the spectrometer used has been described previously⁽¹¹⁾.

During the period τ , the effective Hamiltonian acting on each proton pair is

$$H(\tau) = \frac{\gamma_H^2}{2r_{12}^3} (1 - 3 \cos^2 \theta_{12}) (3I_{z1} I_{z2} - \vec{I}_1 \cdot \vec{I}_2) + H_D (\text{inner}) \\ + (\Delta\omega + \sigma_{zz1}) I_{z1} + (\Delta\omega + \sigma_{zz2}) I_{z2} \quad (1)$$

where θ_{12} is the angle between the vector joining the two protons and the direction of the external magnetic field, σ_{zz1} and σ_{zz2} are chemical shifts, $\Delta\omega$ is the off-resonance term, and $H_D (\text{inner})$ is the portion of the dipolar Hamiltonian that couples the proton pair with the other proton pairs in the system. $H_D (\text{inner})$ is small enough to be ignored here as will be demonstrated below, and the remaining terms commute. This is important because it means that the developments due to each can be separated. Thus, one could refocus the I_z Hamiltonian (chemical shifts and off-resonance effects) for the period, τ , by placing a 180° rf pulse at $\frac{\tau}{2}$. This would be necessary if the chemical shift

anisotropy were comparable in size to the dipolar interaction as it was in the heteronuclear case^(1,6,7). However, here the chemical shift anisotropy is twenty times smaller than the dipolar interaction and a refocusing pulse was not used. However, without the refocusing pulse, it is necessary to correct for the effects of the off-resonance Hamiltonian during the period, τ . Therefore, a linear phase correction was measured on a liquid water sample, and that correction was applied to all spectra to compensate for the presence of the off-resonance Hamiltonian during the time, τ . In addition, there is an amplitude reduction that occurs when the precessional axis for the off-resonance Hamiltonian changes from the (0,0,1) (z-axis) to the (1,0,1) axis (with the multiple pulse sequence on), and this is accounted for in the computer program used to synthesize theoretical spectra. Thus, one needs to consider only evolution under the dipolar term.

$$\begin{aligned} \bar{H}(\tau) &= \frac{\gamma_H^2}{2r_{12}^3} (1 - 3 \cos^2 \theta_{12}) (3 I_{z1} I_{z2} - I_1 \cdot I_2) \\ &= B (3 I_{z1} I_{z2} - I_1 \cdot I_2) \end{aligned} \quad (2)$$

for the time period, τ . This Hamiltonian produces a linear oscillation of the proton magnetization vector at a frequency, $3B/2$, which depends upon the orientation of the dimer. Since the chemical shift is also orientation-dependent, protons with different chemical shifts can exhibit different dipolar oscillation frequencies.

During the second evolutionary period, t , the effective Hamiltonian takes the form⁽⁸⁻¹⁰⁾;

$$H(t) = \frac{\alpha}{3} \left[(\Delta\omega + \sigma_{zz1}) (I_{x1} + I_{z1}) + (\Delta\omega + \sigma_{zz2}) (I_{x2} + I_{z2}) \right] + \dots$$

(higher-order terms) (3)

where α is the chemical shift scaling factor determined experimentally by observing the off-resonance scaling⁽⁸⁾ for a liquid sample. A Fourier-transform of time development under this Hamiltonian will sort the various components of the magnetization according to their chemical shifts, and it will be possible to determine the degree of dipolar modulation taking place for each value of chemical shift.

To furnish a basis for detailed interpretation of dipolar-modulated chemical shift powder patterns taken in this fashion, theoretical powder patterns are created by numerically integrating a series of Lorentzian-broadened isochromats representing an isotropic distribution of crystals. That is, theoretical spectra, $f(\omega, \tau)$, are created by evaluating:

$$f(\omega, \tau) = \int_0^{2\pi} \int_0^{\pi} \cos(\Omega(\theta, \phi)\tau) \left[1 - \frac{1}{2} \sin^2(\omega(\theta, \phi)\tau) \right]^{\frac{1}{2}} \times \{ (\omega(\theta, \phi) - \omega)^2 / w^2 + 1 \}^{-1} \sin\theta d\theta d\phi \quad (4)$$

where one has

$$\Omega(\theta, \phi) = \frac{3}{2} \frac{\gamma_I^2}{r^3} \times \{ 1 - 3(\sin\chi \sin\theta \cos(\phi - \psi) + \cos\chi \cos\theta)^2 \} \quad (5)$$

and

$$\omega(\theta, \phi) = \{ \Delta\omega + \omega_0 (\sigma_x \sin^2\theta \cos^2\phi + \sigma_y \sin^2\theta \sin^2\phi + \sigma_z \cos^2\theta) \} \frac{\sqrt{2}}{3} \alpha \quad (6)$$

where α is the empirically determined off-resonance scaling factor of the eight-pulse cycle⁽⁸⁾, $\Delta\omega$ is the off-resonance frequency, ω_0 is the Larmor frequency of the protons, $(\sigma_x, \sigma_y, \sigma_z)$ are the principal components of the proton chemical shift tensor, (χ, ψ) are the polar angles of the I-I vector with respect to the chemical shift frame, r is the length of the I-I vector, and (θ, ϕ) are the polar angles of external magnetic field in the chemical

shift frame. The parameter w in Equation (4), is the half-width of the Lorentzian broadening function. The expression in square brackets $\left[1 - \frac{1}{2} \sin^2(\omega(\theta, \phi)\tau)\right]^{\frac{1}{2}}$ is the frequency-dependent, amplitude correction factor necessary since a 180° refocusing pulse was not used at $\tau/2$. The factor is a first-order approximation to the reduction in amplitude of a particular isochromat that occurs when the precessional axis changes discontinuously from the z -axis to the $(1,0,1)$ axis as the multiple pulse sequence is turned on at $t = 0$.

While it may appear that there are numerous variables to be obtained from fitting such calculated spectra to the experimental spectra, the system is, in fact, overdetermined. For instance, the normal chemical shift powder pattern serves to determine σ_x , σ_y , σ_z , $\Delta\omega$, and w , leaving only values of r , χ , and ψ to be determined by all other experimental spectra. Thus, any one of the dipolar-modulated chemical shift spectra should furnish the orientation of the proton vector in the chemical shift principal axis frame, and succeeding spectra should furnish only a means to confirm these values. The comparison of values of χ and ψ obtained by a nonlinear, least-squares fitting of experimental spectra with Equation (4) is discussed below.

RESULTS AND DISCUSSION

CCl_3COOH dimerizes in the solid state and crystallizes in a monoclinic structure, space group $P2_1/c$. All protons occupy equivalent sites, although there are two crystallographically distinct dimers per unit cell, and, thus, the polycrystalline pattern could be that of a single proton chemical shift tensor. The relevant part of the CCl_3COOH solid state structure is illustrated in Figure 3, where the dimensions are taken from the neutron diffraction study of Jönsson and Hamilton⁽¹²⁾. The hydroxyl bond is not parallel to the $0--0$ direction

(O-H--O angle of 176.5°), and the ring formed by the two hydrogen-bonding carboxyl groups is essentially planar with no atom out of the plane by more than 0.01 \AA . An inversion point exists midway between the two protons in each dimer, and the two hydroxyl groups lie exactly in the same plane. This plane was taken to define a molecular frame coordinate system with the z axis taken as the hydroxyl, O-H, direction; the y axis defined perpendicular to the z, or hydroxyl, direction in this plane; and the x axis defined perpendicular to the plane. This molecular frame coordinate system is illustrated in Figure 3 with the x axis perpendicular to the plane of the figure, and it will be used to discuss the orientation of the proton chemical shift tensor.

The proton pairs in CCl_3COOH are well isolated from one another⁽¹²⁾, and thus the proton NMR spectrum is primarily that of a proton pair. Goldman⁽¹³⁾ reported seeing well-resolved dipolar split doublets in single-crystal samples of CCl_3COOH , and others^(2,14) have used the dipolar doublets to orient such single-crystal samples. Figure 4 is a Fourier-transform of a free-induction decay obtained from a polycrystalline sample of CCl_3COOH . The powder pattern is near that of an idealized proton pair, a folded, axially symmetric tensor powder pattern⁽¹⁵⁾; and the crispness of the outer shoulders indicates the high degree of isolation of the proton pairs. Since the present experiment simply uses the existing dipolar structure, it will be most informative in such materials which contain small groups of magnetically isolated nuclei.

Figures 5 and 6 illustrate computer fits of theoretical spectra to four of the experimental spectra. All spectra use the reported⁽²⁾ values of σ_x , σ_y , σ_z (-18.2 , -21.8 , and -0.9 ppm relative to a spherical tetramethylsilane sample), and the values of χ and ψ obtained are shown in Table 1. In general, the data taken for dipolar-modulation times, τ , up to 60 microseconds fit the theoretical expression in Equation (4) to within the experimental scatter of

the data, and the fitting parameters were consistent from spectra to spectra. However, for times longer than 70 microseconds, Equation (4) would not fit the spectra without changes in the parameters, and for the spectra with the longest values of τ , Equation (4) predicted qualitatively different spectra with much more detailed structure. We suspect that one needs to consider explicitly the contributions of $H_D(\text{inner})$ for the longer dipolar oscillation times, much as was necessary in the case of heteronuclear dipolar-modulated chemical shift spectra. (There the effects of next-nearest neighbors in benzene became noticeable at dipolar-modulation times of 100-150 microseconds^(1,6,7).) As indicated, χ and ψ are polar angles locating the proton-proton vector in the principal axis system of the chemical shift tensor defined above; thus, χ is the angle between the proton-proton vector and σ_z (the -0.9 ppm principal value), and ψ is the angle between the projection of the proton-proton vector on the σ_x, σ_y plane and the σ_x axis (the -18.2 ppm principal value). Since σ_x and σ_y are very close to one another in value and the proton chemical shift tensor is nearly axially symmetric, the spectra show only a weak dependence on ψ and that angle is not well-determined. (One notes that for a truly axially symmetric pattern, ψ would be undefined and meaningless.) The value for χ is found to be $106.6^\circ \pm 1^\circ$ for each of the spectra. To illustrate the sensitivity of the dipolar-modulated spectra to the relative orientation of the proton-proton vector, two additional spectra have been plotted in Figure 6. The curve fitting the spectrum was obtained with the $\chi = 106.6^\circ$ while the two additional lines show spectra predicted if only the χ value is changed $\pm 3^\circ$ (i.e., 103.6° and 109.6°).

One reason for performing this experiment initially on CCl_3COOH is the existence of single-crystal neutron diffraction structural data⁽¹²⁾ and the

results of a single-crystal rotation multiple pulse NMR study to determine the proton chemical shift tensor⁽²⁾. The single-crystal rotation study found two possible orientations for the proton chemical shift tensor in the molecular frame defined in Figure 3. The ambiguity in the single-crystal study occurred because there are two CCl_3COOH dimers per unit cell, and it is not possible in the single-crystal study to tell which of the two lines observed goes with which dimer. In the present experiment a different type of ambiguity occurs when one attempts to use the information obtained on the relative orientation of the proton-proton vector in the chemical shift principal axis frame to locate the principal axis frame relative to the molecular frame defined in Figure 3. That is, the location of the principal axis frame is known only relative to one molecular frame vector, the proton-proton vector, and can be rotated around the proton-proton vector to different locations relative to the molecular frame of Figure 3. Thus, in the single-crystal case one measures the chemical shift tensor relative to the crystallographic frame and can have ambiguities when multiple sites exist, while in the present experiment one needs to have measured the location of at least two molecular frame vectors in the principal axis frame before one can define fully the chemical shift frame in the molecular frame.

However, if one combines the results of both the single-crystal study⁽²¹⁾ and the present polycrystalline experiments, one finds a unique orientation for the proton chemical shift tensor in the molecular frame. The comparison is most easily done by using the results from the single-crystal to calculate values of χ and ψ to compare with the present study. Such predicted values of χ and ψ are listed in the lower part of Table 1 for both possible orientations found in the single-crystal study, and one notes that one can get

close agreement between one orientation (solution b)⁽²⁾ and the present study for both χ and ψ . Thus, one finds that σ_z ($\sigma_z = -0.9$ ppm) is in the z-y molecular plane of Figure 3 (within $\pm 2^\circ$) and tilted $\sim 3^\circ$ toward the nearest Cl carbon while σ_x ($\sigma_x = -18.2$ ppm) is out of the z-y plane by approximately 20° (with a large error, say $\pm 10^\circ$). Therefore, σ_y (the most negative of the principal values, -21.8 ppm) is 10° from the perpendicular to the z-y plane.

SUMMARY AND CONCLUSIONS

Methods to produce a homonuclear dipolar modulation of a chemical shift powder pattern have been demonstrated and analyzed to furnish the orientation of a vector joining the dipolar-coupled spins in the principal axis frame of the chemical shift tensor. The experiment has been demonstrated for the hydrogen-bonded protons in a model compound, CCl_3COOH , where both structural and proton chemical shift information is available. Orientational parameters obtained by fitting theoretical lineshapes to the experimental data were found to be consistent for dipolar-modulation time less than ~ 70 microseconds and agreed with one of two possible orientations for the proton chemical shift tensor in CCl_3COOH furnished by single-crystal rotation experiments⁽²⁾. Thus, the present experiments not only confirm the utility of the homonuclear dipolar-modulation experiments for furnishing structural information in a polycrystalline solid but, in fact, furnish information not obtainable from the single-rotation studies which allow a definite assignment of the orientation of the proton chemical shift tensor principal axis frame in CCl_3COOH . This experimental scheme should prove particularly useful in systems containing small groups of isolated spin $\frac{1}{2}$ nuclei, a situation common with hydrogen in many solids, and furnishes a means of obtaining orientation information from polycrystalline samples.

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TABLE 1. Orientation of Proton-Proton Vector
in Chemical Shift Principal Axis Frame

Spectrum #	τ (μsec)	χ	ψ
1	4.2	-	-
7	29.2	106.7°	28°
10	41.7	105.6°	24°
16	66.7	107.6°	13°
Average		$106.6^\circ \pm 1^\circ$	$20^\circ \pm 8^\circ$
Single Crystal Results ^a			
for solution (a)		$89^\circ \pm 2^\circ$	$0 \pm 20^\circ$
for solution (b)		$107.4^\circ \pm 2^\circ$	$0 \pm 20^\circ$

^afrom reference 2.

FIGURE CAPTIONS

- Figure 1. Schematic diagram of rf pulse sequence used. A 90° prepulse is given and followed by the period of dipolar evolution τ . From time $t = 0$, the eight-pulse cycle is applied to the protons to remove the homonuclear dipolar interaction.
- Figure 2. Homonuclear dipolar-modulated proton chemical shift spectra in polycrystalline CCl_3COOH . The numbers indicate the length of dipolar evolution time, τ , in units of $4.17 \mu\text{sec}$. The spectra show the observed relative intensities although those on the right have been vertically magnified for clarity. On the horizontal axis, each channel represents $.71 \text{ ppm}$. The proton resonance was at 56.4 MHz .
- Figure 3. Carboxylic structure of CCl_3COOH dimers in the solid state. Indicated bond distances and bond angles are as determined in Reference 9. A molecular frame of reference is defined in which the z axis is parallel to the hydroxyl direction, the y axis in the plane determined by the two hydroxyl groups of the dimer and perpendicular to the z axis, and finally the x axis is defined perpendicular to both of these and in the direction to furnish a right-handed coordinate system. The x axis is directed up out of the figure.
- Figure 4. Fourier-transform of proton free-induction decay in polycrystalline CCl_3COOH . Each horizontal channel represents 488 Hz .

Figure 5. Theoretical fits (solid lines) to three of the homonuclear dipolar-modulated proton chemical shift spectra (points) from Figure 2. The number near each spectrum designates, when multiplied by 4.17, the dipolar evolution time, τ , in microseconds and the parameters obtained from the fitting program are listed in Table 1. The horizontal scale is 0.71 ppm/pt, and the bottom two spectra have been magnified vertically by factors of 2 and 5, respectively, compared with top spectrum. The experimental spectra are presented in Figure 2 with the proper relative normalization.

Figure 6. The experimental spectrum (points) for a dipolar-modulation time of 66.7 microseconds compared with a theoretical fit (solid line). As in Figure 5 the horizontal scale is 0.71 ppm/point. The two additional lines placed through the data are to illustrate the sensitivity of the shape of the spectra to small deviations in the angle, χ , between the σ_z and the proton-proton vector. To obtain these additional curves all parameters found for the solid line were fixed except for χ , which was altered by $\pm 3^\circ$ for the two curves.

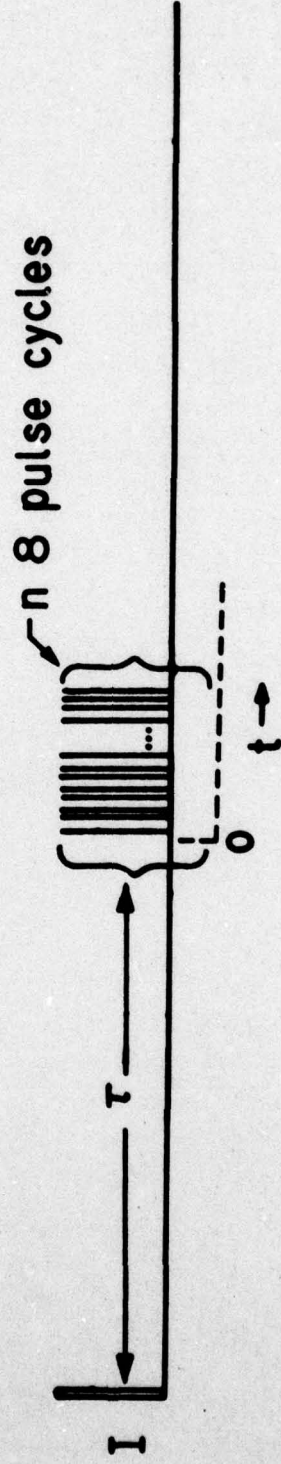


Figure 1

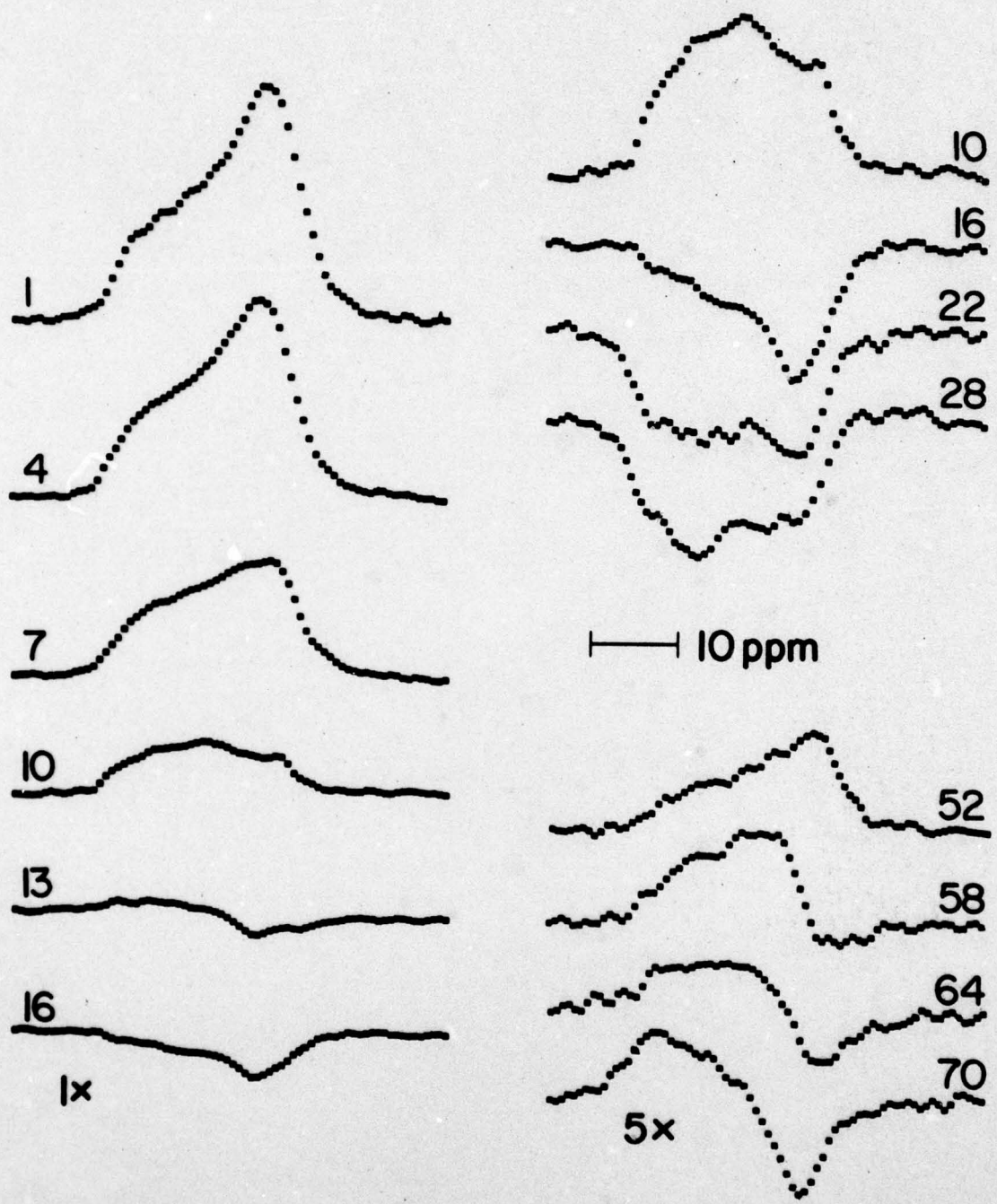


Figure 2

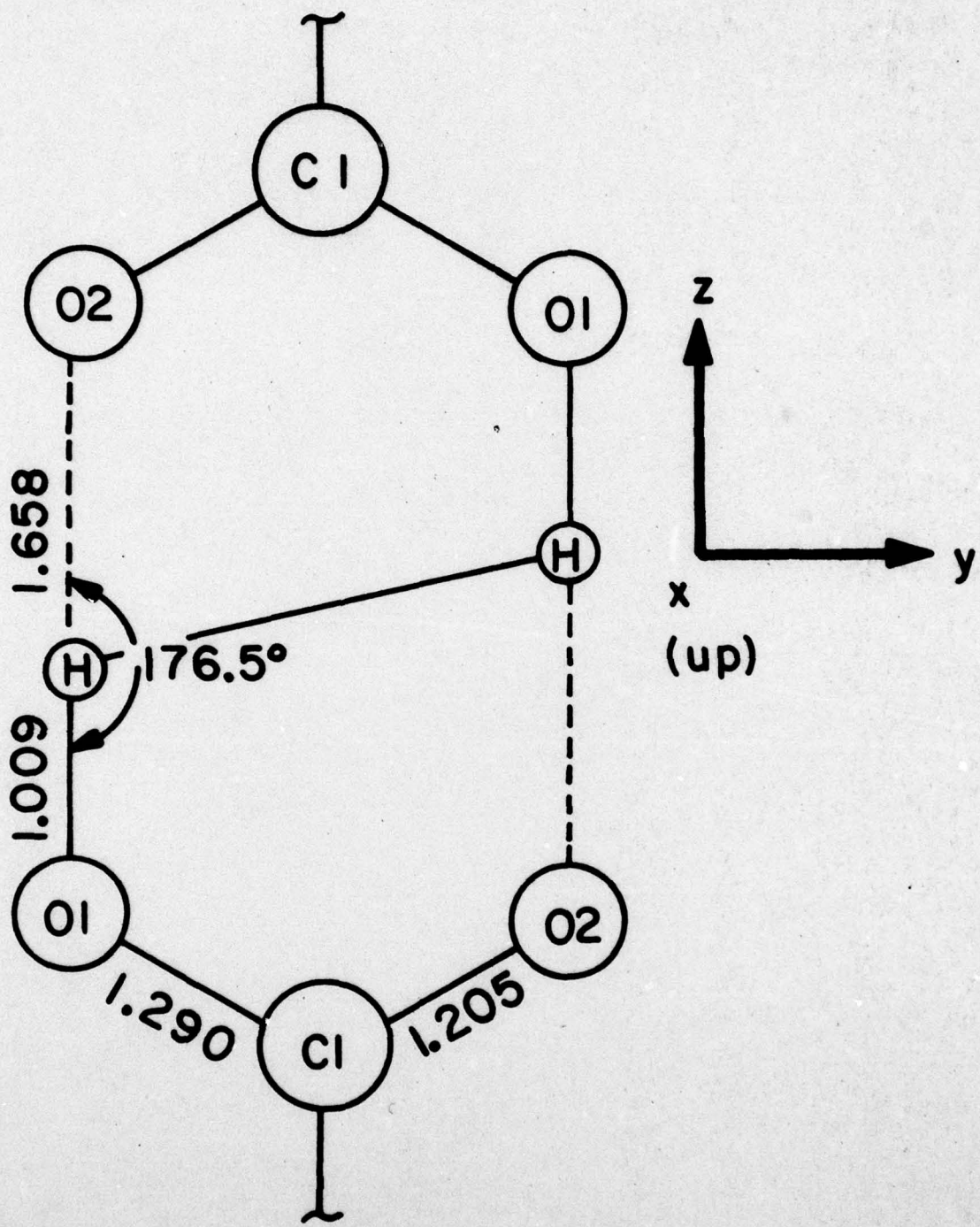


Figure 3

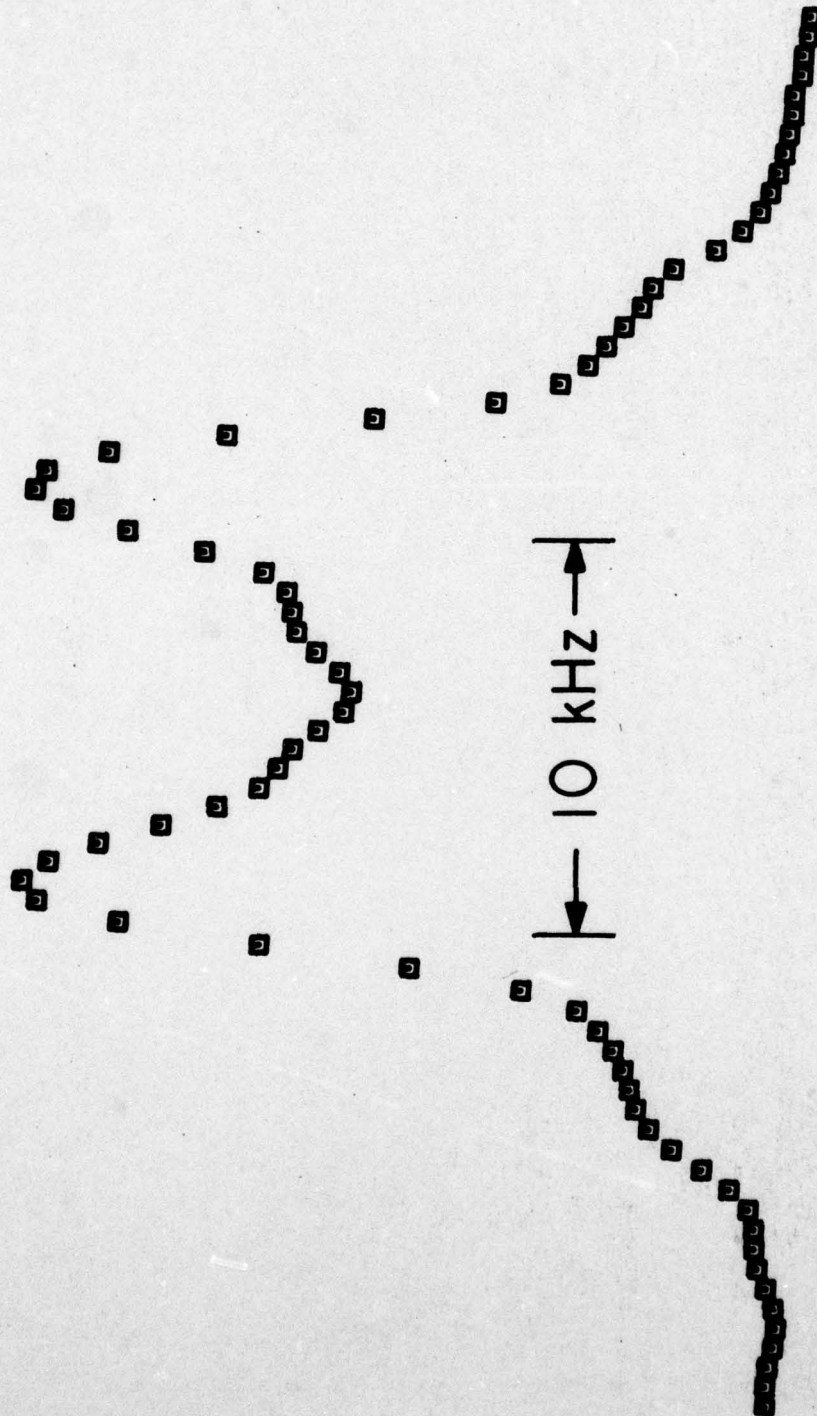


Figure 4

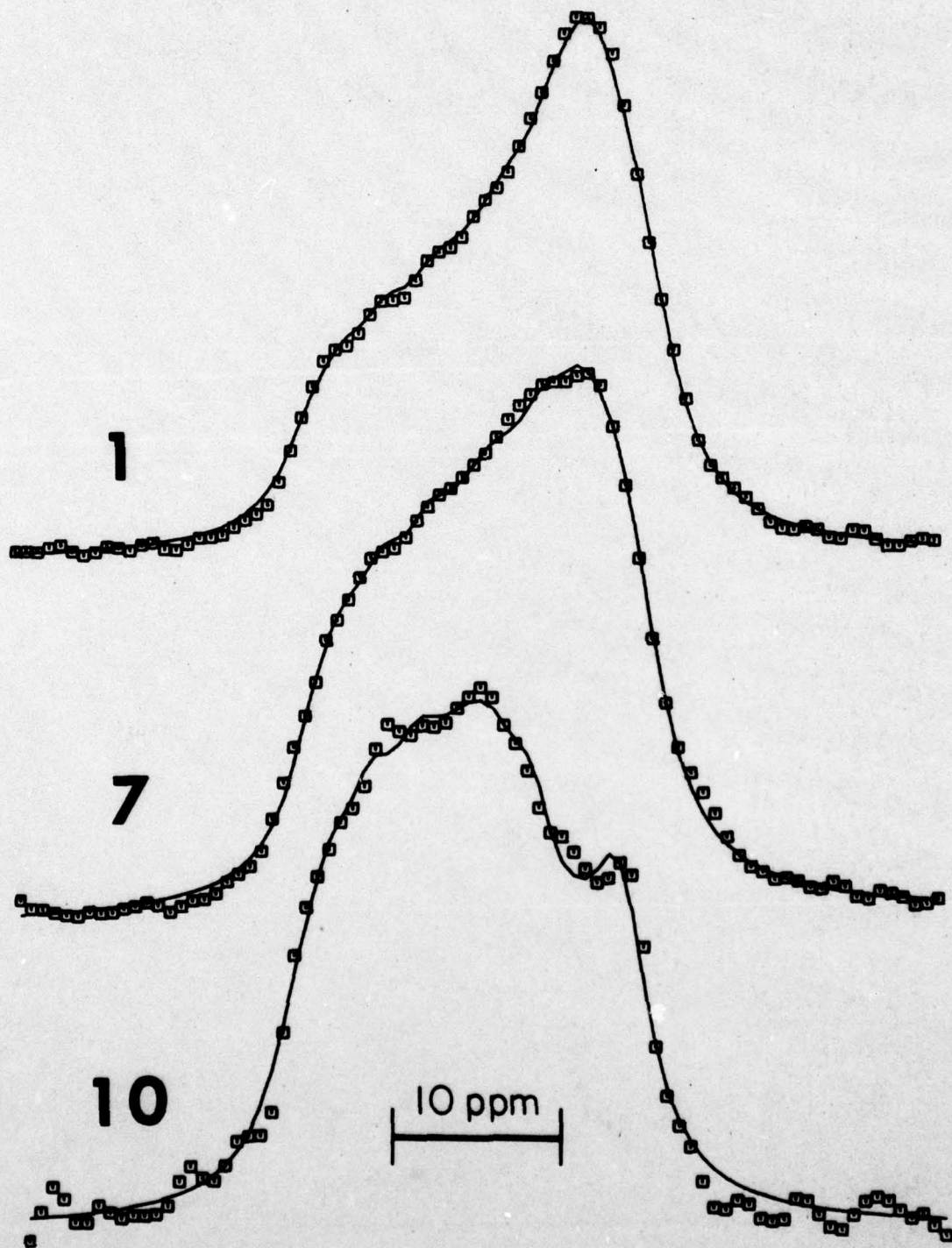


Figure 5

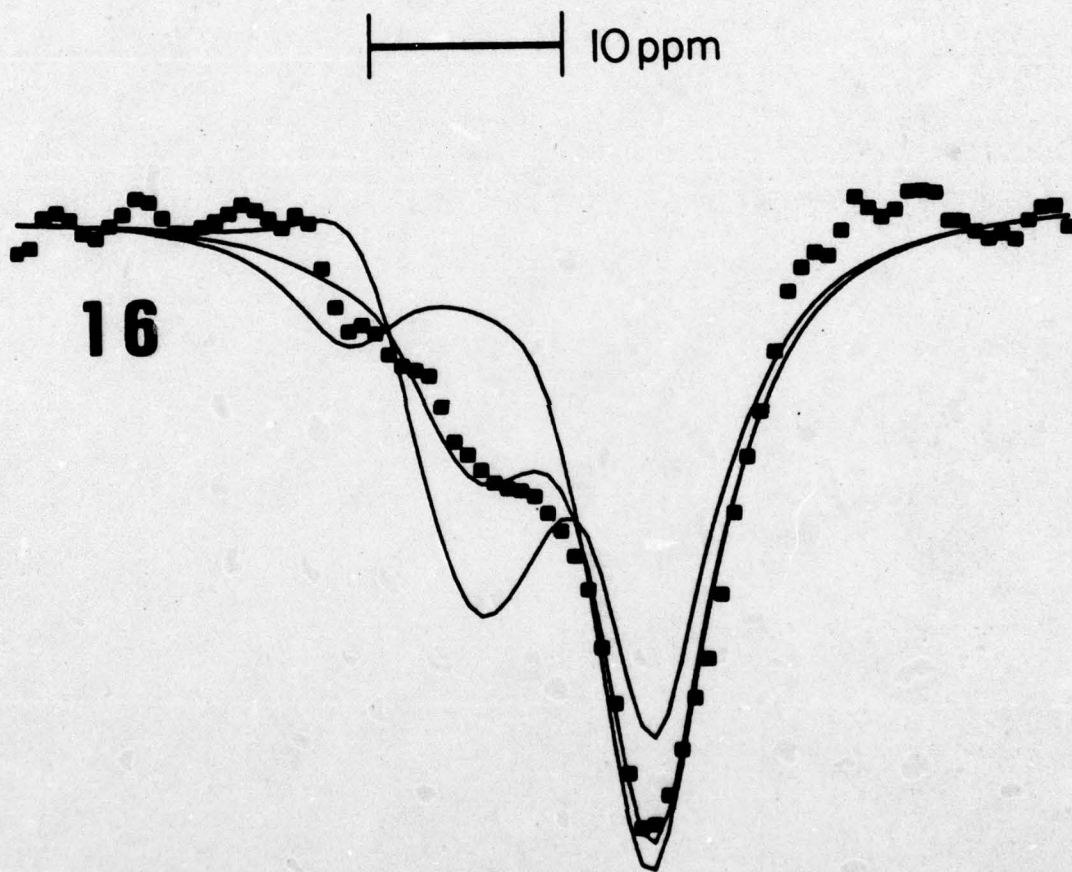


Figure 6

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