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G. Drobny, A. Pines, S. Sinton, D. Weitekamp, and D. Wemmer

December 1978

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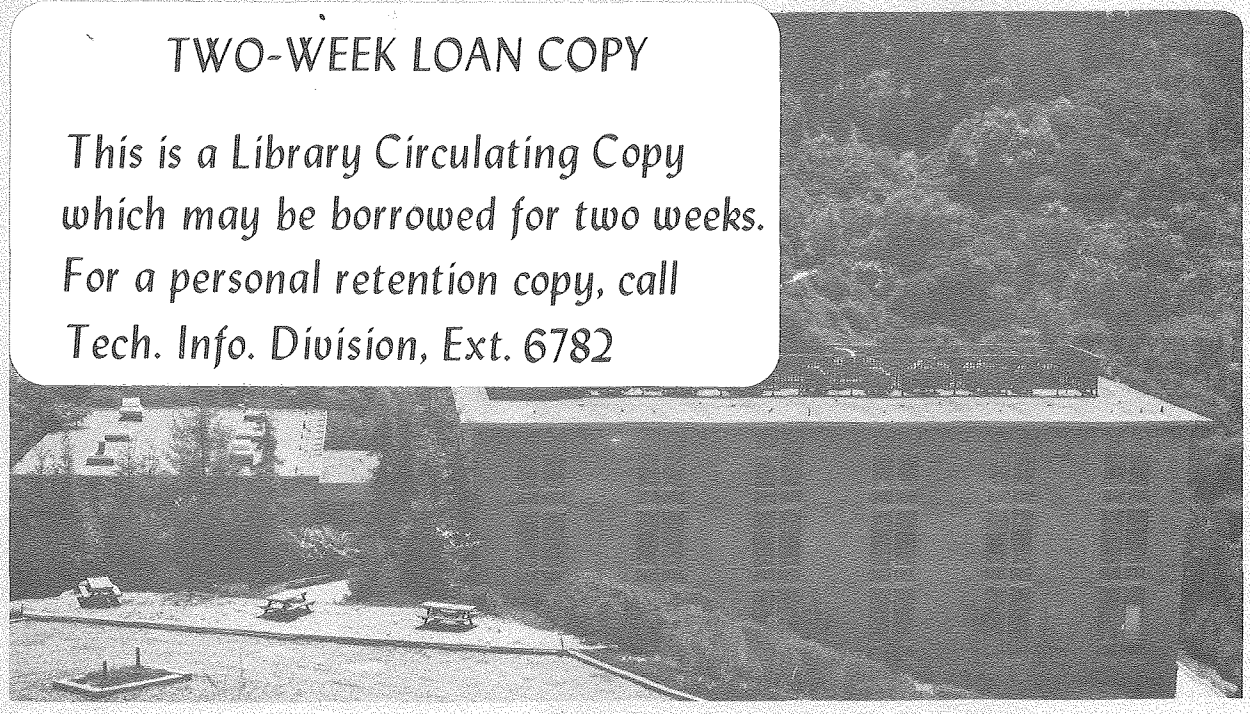

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FOURIER TRANSFORM MULTIPLE QUANTUM NMR

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The excitation and detection of multiple quantum transitions in systems of coupled spins offers, among other advantages, an increase in resolution over single quantum NMR, since the number of lines decreases as the order of the transition increases. This paper reviews the motivation for detecting multiple quantum transitions by a Fourier transform experiment and describes an experimental approach to high resolution multiple quantum spectra in dipolar systems along with results on some protonated liquid crystal systems. A simple operator formalism for the essential features of the time development is presented and some applications in progress are discussed.

Experimental

The spectrometer is of pulsed Fourier transform design with superconducting magnet (Bruker) operating in persistent mode at a proton frequency of 185 MHz. Phase shifting was performed at 185 MHz by a digitally controlled device (DAICO 100D0898) under control of the pulse programmer.

Samples were approximately 400 mg sealed in 6mm glass tubing after degassing by repeated freezing and evacuation. All observations are in the nematic phase. Synthesis of 4-cyano-4'-pentyl-d_{11}-biphenyl was by the procedure of Gray and Mosley.[1]

The energy level diagram of a system of coupled spins 1/2 in high

field is shown schematically in Fig. 1. The eigenstates are grouped according to Zeeman quantum number m_i with smaller differences in energy within a Zeeman manifold due to the couplings between spins and the chemical shifts. For any eigenstate $|i\rangle$ of the spin Hamiltonian H (in frequency units)

$$\begin{aligned} H\,|i\rangle &= \omega_i\,|i\rangle \\ I_z\,|i\rangle &= m_i\,|i\rangle \end{aligned} \tag{1}$$

The single quantum selection rule[2] of the low power CW experiment and the one dimensional Fourier transform experiment arises because $\langle i|I_x|j\rangle$ vanishes unless

$$q_{ij} = m_i - m_j = \pm 1. \tag{2}$$

Simple combinatorial considerations show that the number of eigenstates decreases as $|m_i|$ increases and the number of transitions decreases as $|q_{ij}|$ increases. The highest order transition possible is the single transition with $|q| = 2I$ where I is the total spin. For a system of N spins 1/2, transitions up to order N are possible.

Detection of multiple quantum transitions in CW experiments is well known.[3-5] Extension to high order transitions is not promising, since the transitions observed are a sensitive function of RF field strength. This leads to difficult spectral simulations and experimental problems of saturation and sample heating.

The alternative time domain experiment is the determination of multiple quantum transition frequencies by following the time development of multiple quantum coherences point by point.[6-8] This work treats a class of such multidimensional experiments in which the irradiation consists of pulses at the Larmor frequency. Time proportional incre-

mentation of the RF phase (TPPI) allows separate determination of the spectra of all orders free from effects of magnet inhomogeneity.

Results

The spectrum of benzene dissolved in a liquid crystal served as a prototype in the development of the single quantum NMR of complex spin systems in ordered phases.[9] The multiple quantum spectrum of ordered benzene is shown in Fig. 2. The resolution is limited by magnet homogeneity and the inhomogeneous linewidth is proportional to $|q|$.

The spectrum of Fig. 3 demonstrates the use of the spin echo to remove inhomogeneous line broadening and the use of time proportional phase increments (TPPI) to restore the offset. Resolution is limited by truncation of the multiple quantum free induction decay and scale of reproduction. The actual linewidth is less than 2Hz for all orders and suffices to resolve all allowed transitions of all orders.

An application of the TPPI method to the eight proton system of an alkyl-deuterated cyano biphenyl liquid crystal is shown in Fig. 4. All eight orders are observed. Resolution is limited by truncation. Actual linewidths are less than 100 Hz in a spectral width of about 40 kHz for each order.

Discussion

The Three Pulse Experiment

The time development of the spin system during the pulse sequences of Fig. 2 and 3 is conveniently discussed in terms of a spherical tensor operator expansion of the density matrix. For any time,

$$\rho(t) = \sum_{k,\alpha,q} C_q^{k\alpha}(t)\, T_q^{k\alpha} \qquad (3)$$

where T_q^k is the q^{th} component of a spherical tensor operator of rank k.[10] The label α completes the specification of a complete basis of tensor operators.

The initial equilibrium density matrix is

$$\rho(0) = C_o^{1I}(0)I_z = C_o^{1I}(0)T_o^{1I} \tag{4}$$

and immediately after a $\pi/2_y$ pulse ($\omega_1 >> H, \omega_1 t_{P1} = \pi/2$)

$$\rho(t_{P1}) = -C_o^{1I}(0)I_x = C_1^{1I}(t_{P1})T_1^{1I} + C_{-1}^{1I}(t_{P1})T_{-1}^{1I} \tag{5}$$

The Zeeman quantum number q is conserved during evolution under a high field Hamiltonian. Thus neglecting relaxation

$$\rho(t) = \sum_{k,\alpha,\pm 1} C_q^{k\alpha}(t)T_q^{k\alpha} \tag{6}$$

at any time t after the initial $\pi/2$ pulse and no multiple quantum coherence has been created. After a period of time on the order of the inverse of the coupling frequencies, terms with $k \leq 2I$ will be present. A second strong pulse may then rotate $T_{\pm 1}^{k\alpha}$ into $T_q^{k\alpha}$ with $-k \leq q \leq k$. Thus at time τ, after the second pulse, all orders with $-2I \leq q \leq 2I$ have, in general, been created and evolve during the time t, at the eigenfrequencies $\omega_{ij} = \omega_i - \omega_j$.

If the only observable measured is the transverse magnetization corresponding in the rotating frame to the $|q| = 1$ operators I_x and I_y, it is not possible to follow the evolution of orders with $|q| \neq 1$ directly. Rather, a third pulse at time t_1 after the second pulse is needed to rotate the various tensor components back to $T_{\pm 1}^{k\alpha}$. These may then evolve into signal observed at time t_2 after this detection pulse.

The signal may be written then as

$$S(\tau, t_1, t_2) = C_o^{1I}(0)T_r(I_+\rho(\tau + t_1 + t_2)). \tag{7}$$

Viewed as a function of t_1 this is the multiple quantum free induction decay. It is collected pointwise by variation of t_1 on successive shots and is an example of a multidimensional NMR experiment.

Separation of Orders by Frequency Offset

In order to obtain an increase in resolution over the single quantum experiments it is necessary to separate the spectra of different order. Consider the decomposition of the density matrix at time τ ($t_1 = 0$) into Zeeman components

$$\rho(\tau) = \sum_{q=-2I}^{2I} \rho_q(\tau) \qquad (8)$$

By construction, $\rho_q(\tau) = \sum_{k\alpha} C_q^{k\alpha}(\tau) T_q^{k\alpha}$ and it follows from the definition of the spherical tensor operators that

$$\rho_q(\tau,\phi) = \exp(i\phi I_z)\rho_q(\tau)\exp(-i\phi I_z) = \exp(iq\phi)\rho_q(\tau) \qquad (9)$$

If we let $\phi = \Delta\omega t_1$, then eq. (9) corresponds to a calculation of the effect of a frequency offset term $-\Delta\omega I_z$ in the rotating frame Hamiltonian. Thus a modulation by $\exp(iq\Delta\omega t_1)$ is caused by the offset, shifting the spectrum to $q\Delta\omega$ as seen in Fig. 2.

The difficulty with this approach to separation of orders is that the effect of magnet inhomogeneity is proportional to $|q|$. The sample volume at position $\vec{r}$ with offset $\Delta\omega(\vec{r})$ contributes a term $\rho_q(\tau,t_1,\vec{r}) = \exp(iq\Delta\omega(\vec{r})t_1)\ \rho_q(\tau+t_1)$ and integration over $\vec{r}$ leads to damping of the coherence with a time inversely proportional to $|q|$.

High Resolution Spectra by Time Proportional Phase Increments (TPPI)

The Hahn spin echo technique may be used to remove the inhomogeneous broadening. A π pulse at $t_1/2$ changes q to -q, allowing a refocusing of the coherence at t_1 for all orders. However this π pulse also removes the

separation of the orders which was a result of the frequency offset.

A solution to this dilemma is to view eq. (9) not as the effect of a frequency offset, but as a shift of the RF phase. In particular, consider the effect of preparing the system with pulses of phase ϕ and $\bar{\phi} = \phi + \pi$ at time zero and τ respectively, with $I_\phi = I_x \cos\phi - I_y \sin\phi$. Then

$$\begin{aligned}
\rho(\tau,\phi) &= \exp(i\theta I_\phi)\exp(-iH\tau)\exp(-i\theta' I_\phi)\ x \\
&\rho(0)\exp(i\theta' I_\phi)\exp(iH\tau)\exp(-i\theta I_\phi) \\
&= \exp(i\phi I_z)\exp(i\theta I_x)\exp(-iH\tau)\exp(-i\theta' I_x)\ x \\
&\rho(0)\exp(i\theta' I_x)\exp(iH\tau)\exp(-i\theta I_x)\exp(-i\phi I_z) \\
&= \exp(i\phi I_z)\rho(\tau)\exp(-i\phi I_z) \\
&= \sum_q \exp(iq\phi)\rho_q(\tau) \qquad (10)
\end{aligned}$$

The result is that again

$$\rho_q(\tau,\phi) = \exp(iq\phi)\rho_q(\tau)$$

but this modulation is now an artifact of the RF phase of the first two pulses and does not depend on the evolution of the system during t_1. However, since each point t_1 of the signal is collected separately, we may set $\phi = \Delta\omega t_1$ for some parameter $\Delta\omega$, thereby recovering an apparent offset.

The actual evolution during t_1 may include an echo pulse to remove the effect of field inhomogeneity, as in Fig. 3, or a train of π pulses to remove the effect of small chemical shifts and heteronuclear couplings from the dipolar spectra.

This TPPI technique may be compared to the method of phase Fourier transformation (PFT) discussed elsewhere.[11,12] The PFT method generates a signal array $S(\tau,t_1,t_2,\phi)$ by repeating the experiment for each t_1 and ϕ, where again ϕ describes the phase of the preparation pulses as in eq. (11).

Fourier transformation with respect to phase with q as the conjugate variable separates the orders. A second Fourier transformation with respect to t_1 gives the spectra. In the TPPI experiment the phase and time dimensions are collapsed into one by the relation $\phi = \Delta\omega t_1$. A single time Fourier transformation gives the spectrum of each order with apparent offset $q\Delta\omega$ as in Fig. 3 and Fig. 4.

Multiple Quantum Spectroscopy of Liquid Crystals

Although the spectroscopy discussed is of general applicability, it is worthwhile to note the particular suitability of the MQFTNMR method to the study of liquid crystals. The diffusion present in such systems sharply reduces the intermolecular dipolar couplings. This allows one to obtain resolved spectra reflecting only the intramolecular couplings without dilution of the spin system. Combinatorial arguments suggest that it suffices in general to analyze only the $|q| = N-2$ and $N-1$ spectra to determine all couplings in a system of N spins 1/2. Since these transitions involve only the relatively small $|m| = \frac{N}{2}, \frac{N}{2}-1$, and $\frac{N}{2}-2$ Zeeman manifolds of the basis of kets, the diagonalizations are simpler than those needed for single quantum spectroscopy. Should the study of mixtures be of interest, partial deuteration of the background species will reduce its contribution to the high order spectra more rapidly than to the single quantum spectrum and thus the requirement for isotopically pure synthesis is reduced.

Applications in progress include the configurational analysis of both ring and chain regions of liquid crystals, the study of relaxation effects in multiple quantum spectra, and improvement of signal to noise by removal of the dipolar Hamiltonian during detection and sampling of

magnetization at many times t_2.

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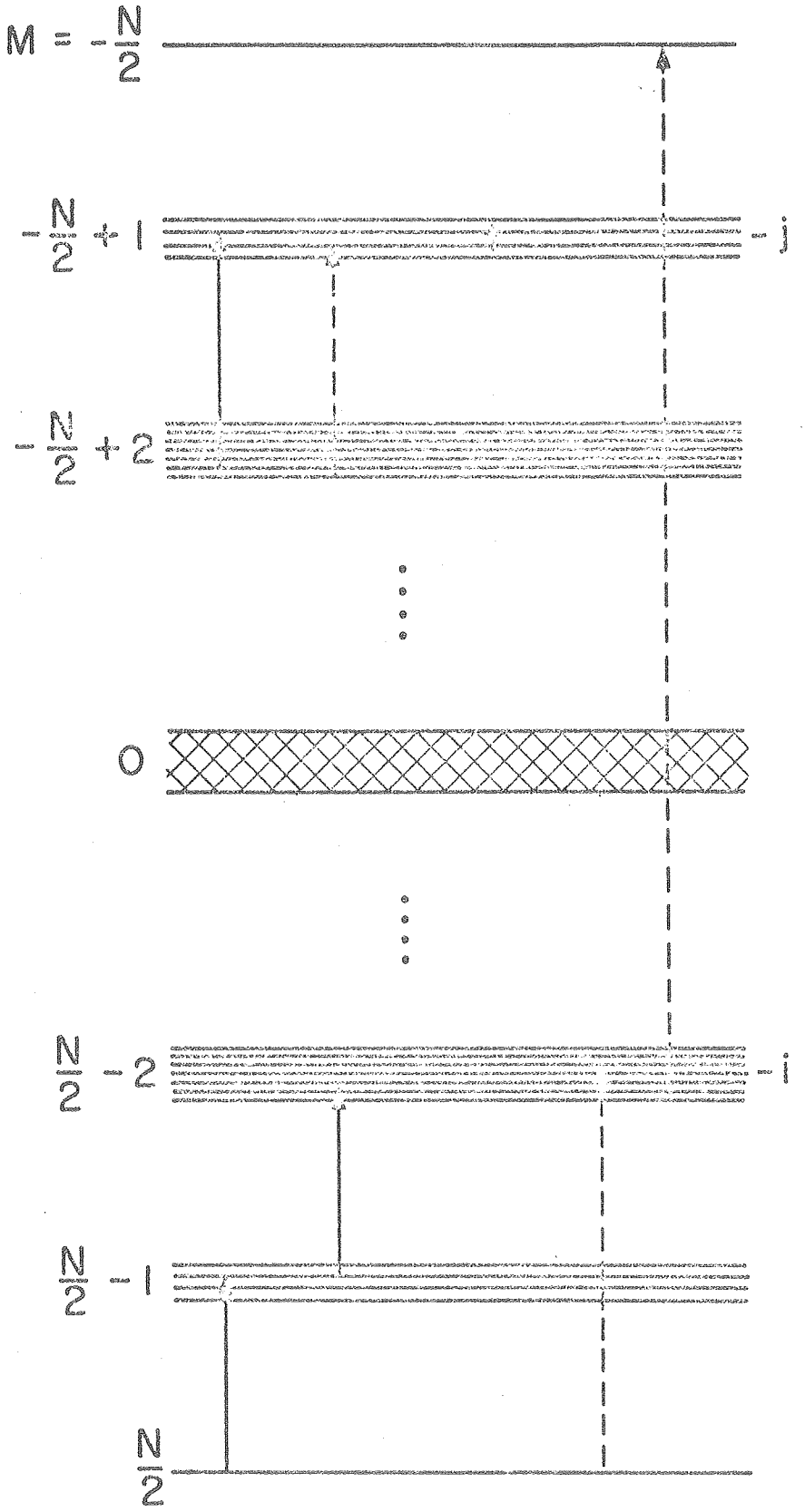
Figure Legends

Fig. 1 Schematic representation of the high field energy level diagram of coupled spins 1/2. Broken arrows indicate the forbidden types of transition observed in Fourier transform multiple quantum experiments.

Fig. 2 Multiple quantum spectrum of benzene (15 mole percent) in p-ethoxybenzylidene-n-butylaniline (EBBA) at 20°C. The three pulse sequence was P1 = $\pi/2_x$, P2 = $\pi/2_{\bar{x}}$, P3 = $\pi/2_x$. The magnitude spectra obtained for 11 values of τ spaced at .1 msec intervals from 9.6 to 10.7 msec were added. The value of t_1 ranged from 0 to 13.824 msec in 13.5 μsec increments for each τ. A single sample point was taken at $t_2 = \tau$ after P3. One half of a symmetrical spectrum is shown.

Fig. 3 Multiple quantum spectrum of benzene at 22°C and TPPI pulse sequence. The sample is the same as in Fig. 2. The pulses are P1 = $\pi/2_\phi$, P2 = $\pi/2_{\bar{\phi}}$ and P3 = $\pi/2_x$, where $\phi = \Delta\omega t_1$. The increment was 29.5 degrees in ϕ and 10 μsec in t_1 for each of 1024 points. The magnitude spectra for eight values of τ between 9 and 12.5 msec were added. The magnetization was sampled at $t_2 = \tau$.

Fig. 4 Proton multiple quantum spectrum of 4-cyano-4'-pentyl-d_{11}-biphenyl at 23.3°C by TPPI. The increments are 22.5 degrees in ϕ and 1.5 μsec in t_1 for each of 1024 points. The time τ took five values between .5 and 1.0 msec and the magnetization was sampled at 64 intervals of 5 μsec starting at $t_2 = (\tau - .1)$ msec.



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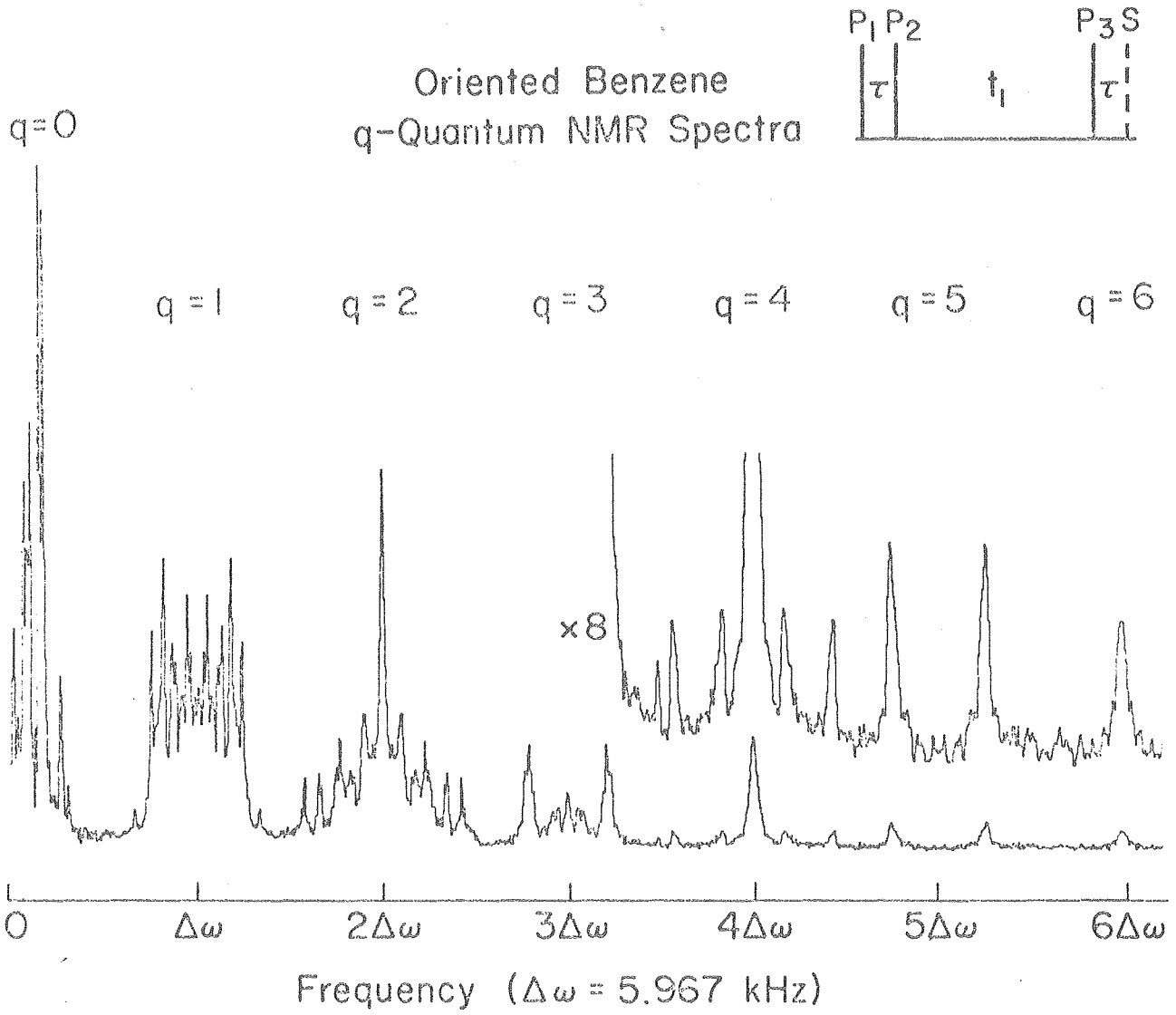

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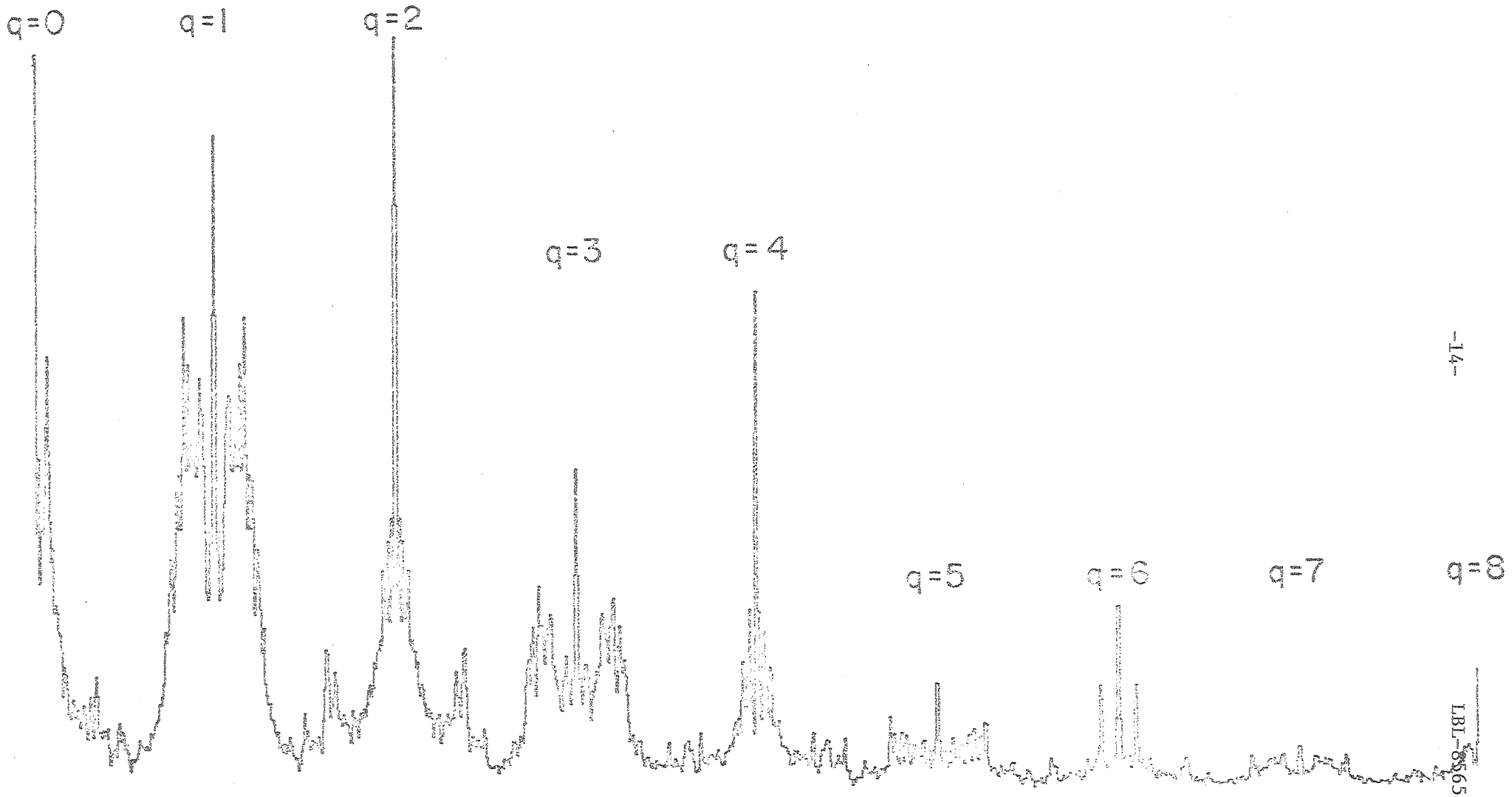
Oriented Benzene
q-Quantum TPPI Echo Spectra
P1 P2 t1/2 E t1/2 E P3 S
q = 0
q = 1
q = 2
q = 3
q = 4
q = 5
q = 6

8-Proton Liquid Crystal

q-Quantum TPPI Echo Spectra



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