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Authors

Garbow, J.R.

Weitekamp, D.P.

Pines, A.

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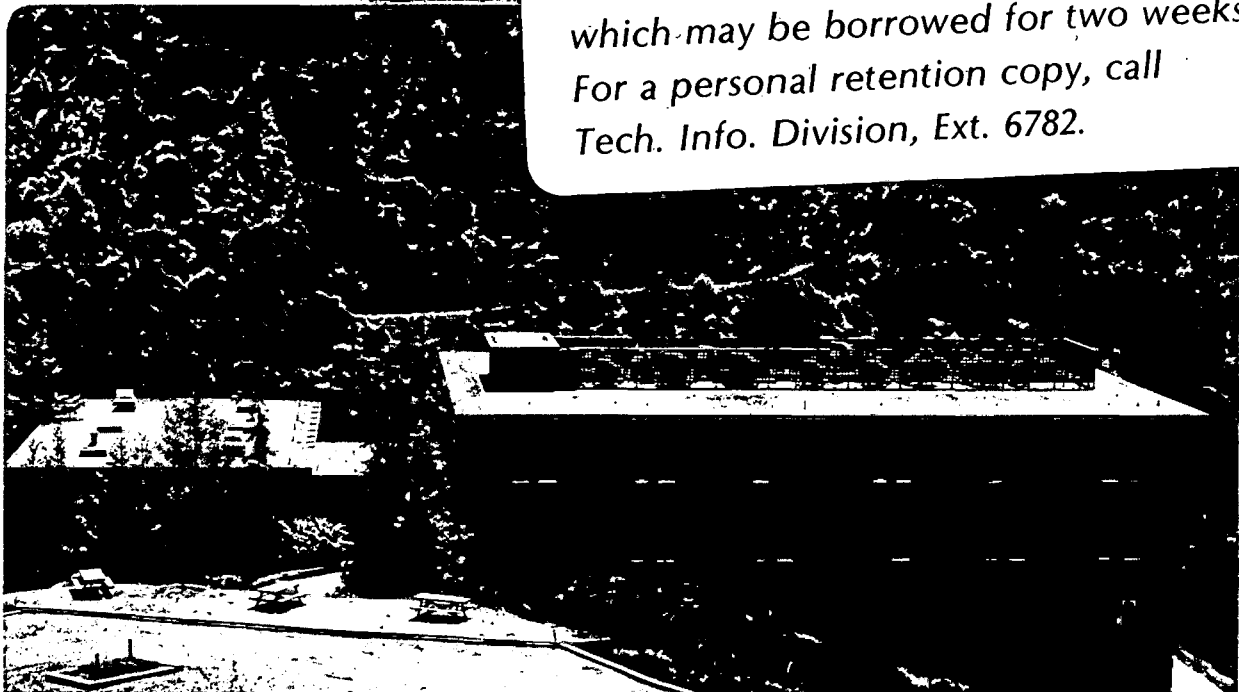
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BILINEAR ROTATION DECOUPLING OF HOMONUCLEAR
SCALAR INTERACTIONS

J. R. Garbow, D. P. Weitekamp, and A. Pines

Department of Chemistry and

Lawrence Berkeley Laboratory

University of California, Berkeley CA 94720

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ABSTRACT

A method for obtaining NMR spectra of organic liquids free of J-couplings is described. The coupling between a group of equivalent protons and an adjacent ^{13}C acts as a local decoupling field for the protons. A pure chemical shift spectrum of ethanol is presented and applications to strongly coupled systems are discussed.

INTRODUCTION

Effective broadband proton homonuclear decoupling is a longstanding problem in the NMR of molecules in solution. The scalar nature of the homonuclear J-coupling renders ineffective the multiple pulse sequences which remove homonuclear dipole couplings in solids state NMR [1-3]. In weakly coupled systems, methods of homonuclear decoupling are known. Spin tickling with a weak r.f. field [4] is possible for well-resolved multiplets. The method of J- δ spectroscopy [5,6] allows extraction of pure chemical shift spectra in weakly coupled systems by manipulation of a two dimensional data array without actual decoupling during the evolution period. In order to decouple a group of equivalent spins from all of its neighbors, one must be able to single out and manipulate that group independently of other spins in the system. In this paper we describe a means for homonuclear decoupling of protons in systems of several protons (I spins) and a randomly positioned ^{13}C (S spin) such as is encountered in natural abundance studies of most organic molecules. The heteronuclear J-coupling between the protons and the carbon spin serves to distinguish the directly bound (satellite) protons from all others. The ^{13}C nucleus can be thought of as a local decoupling field capable of nutating those protons to which it is coupled. The interaction is a product of the I and S spin angular momenta and the method described here is termed Bilinear Rotation Decoupling (BIRD).

EXAMPLE OF HOMONUCLEAR DECOUPLING

As an illustrative example, Figure 1 shows the results of the decoupling experiment performed on samples of 95% ethanol in water. In Figure 1(a) is the familiar proton spectrum of the methyl and methylene groups. In Figure 1(b) we observe these same proton multiplets superimposed upon the much larger splittings due to scalar coupling to a ^{13}C nucleus in an isotopically enriched sample. Figure 1(c) illustrates the BIRD spectrum of the same sample. All multiplet structure has been collapsed, while the chemical shifts are accurately preserved in the positions of the resulting singlet lines.

In recent years the indirect spin-spin coupling between nearby heteronuclear spins in liquids has been used to perform a variety of useful site-selective manipulations. The problems approached include: the transfer of magnetization from one spin species to another [7-10]; creation of heteronuclear multiple quantum coherence [11,12]; observation of ^{13}C satellite proton spectra without interference from the ^{12}C containing groups [13,14]; and the creation of non-equilibrium population distributions (J order) [9,15,16]. All of these experiments resemble one another in that they involve sequences of several strong r.f. pulses of nutation angle $\pi/2$ or π applied to one or both spin species separated by periods of free evolution on the order of $1/J_{IS}$, the inverse of the heteronuclear coupling between the spins of interest. The method of homonuclear coupling described here is related in this regard.

THEORY OF BILINEAR ROTATION DECOUPLING

To understand how the local field of the ^{13}C spin can be used as a decoupling field, we need the concept of a bilinear rotation. The Hamiltonian describing the coupling between a proton and a ^{13}C nucleus may be written in radians/sec as

$$\mathcal{H}_{IS} = J'_{IS} I_z S_z \quad (1)$$

where $J'_{IS} = 2\pi J_{IS}$. When sandwiched between a pair of strong $\pi/2$ pulses on the protons, this Hamiltonian produces a propagator of the form

$$U^p(t) = \exp(-iJ'_{IS} I_p S_z t) \quad , \quad p = x, y \quad (2)$$

which we recognize as describing a rotation about the proton "p"-axis. We term propagators of this form simple bilinear rotations, with the quantity $(1/2)J'_{IS}t$ playing the role of the rotation angle. In particular, when $t = 1/J_{IS}$ the propagator in (2) acts like a π pulse applied to the satellite protons. The pulses required to form a simple bilinear rotation are shown in Figure 2(a). The π pulses applied to both spin species at the midpoint of this sequence serve to make the action of the bilinear rotation insensitive to resonance offsets and chemical shifts of either I or S.

WEAKLY COUPLED SYSTEMS

A single bilinear rotation is sufficient to cause homonuclear

decoupling in weakly coupled systems. Such systems are characterized by chemical shifts and truncated homonuclear spin-spin couplings:

$$\mathcal{H} = -\sum_i \omega_i I_{zi} - \sum_{i < j} J'_{ij} I_{zi} I_{zj} \quad (3)$$

Labeling the satellite proton as "k", we can write the effect of a bilinear π rotation as

$$I_{zk} \rightarrow -I_{zk} \quad (4a)$$

$$I_{zi} \rightarrow I_{zi}, \quad i \neq k \quad (4b)$$

If this bilinear π is followed immediately by a strong proton π pulse, the overall effect is to flip all protons except the one bonded to the ^{13}C .

Fig. 3(a) illustrates the use of the bilinear π pulse and an adjacent strong proton π pulse to give the simplest BIRD pulse sequence. The box labelled U_{π}^x represents either the pulses of Fig. 2(a) or of Fig. (2b)(described below). The experiment is two dimensional in that the signal is sampled (at the point indicated by the broken line) as a function of t_1 , which is incremented on successive shots. Fourier transformation with respect to t_1 gives the spectrum of Fig. 1(c).

In a toggling frame representation [1-3], a homonuclear coupling term $J'_{ik} I_{zi} I_{zk}$ during the first period $t_1/2$ becomes $-J'_{ik} I_{zi} I_{zk}$ in the second period $t_1/2$. The average Hamil-

tonian [1-3] for this spin-spin coupling is zero. Similarly, the heteronuclear coupling vanishes. The chemical shift terms $\omega_k I_{zk}$ for the satellite protons are, however, preserved. Two alternative representations of this experiment using, respectively, energy levels and magnetization vectors are given in Fig. 4.

SUPPRESSION OF LINES FROM CARBON-12 BONDED PROTONS

In practice, a means is needed of suppressing magnetization from protons not adjacent to a ^{13}C . This was done by adopting a recent method, due to Freeman et al. [13], which itself is easily understood in terms of a bilinear rotation. In this method two experiments are performed and their signals combined to give pure satellite spectra such as Fig. 1(b). In the first experiment a bilinear rotation serves to align the satellite and non-satellite magnetizations antiparallel before the f.i.d. is recorded. In the second, the r.f. pulse on the ^{13}C is omitted and the magnetizations start out in phase. Subtraction of the two signals suppresses the non-satellite signal. The same trick is used to obtain Fig. 1(c), but here the BIRD sequence of Fig. 3(a) follows the initial preparation of the magnetizations.

COMPENSATED BILINEAR ROTATIONS

In rotations of the type we have been discussing, the bilinear nutation frequency is proportional to J_{IS} . When two or more different coupling constants J_{IS} are present in a system, it becomes impossible to choose a single time such that all carbon-proton pairs experience

the same flip angle. This is similar to the observed sensitivity of cross polarization efficiency in liquids to the distribution of the scalar couplings [17,18]. Analogy can also be drawn to the situation where a range of chemical shifts, or an inhomogeneity of the static or r.f. fields causes different parts of a sample to experience different r.f. nutations. In analogy to compensated r.f. pulses [19-21], we introduce a compensated bilinear rotation, illustrated in Fig. 2(b). The propagator for this pulse sequence can be written as the product of three propagators, corresponding to alternate rotations about the x and y coordinate axes:

$$\exp(-iJ'_{IS} I_x S_z (2\tau)) \exp(-iJ'_{IS} I_y S_z (4\tau)) \exp(-iJ'_{IS} I_x S_z (2\tau)) . \quad (5)$$

The time τ is chosen to result in a perfect bilinear rotation for some representative spin-spin coupling, J_{IS}^0 ($4\tau = 1/J_{IS}^0$). Compensated bilinear π rotations are much less sensitive than the simple bilinear π of Fig. 2(a) to the inevitable distribution of J_{IS} . As a result, BIRD and other experiments which use bilinear pulses become practical for more diverse molecules.

STRONGLY COUPLED SYSTEMS

It is interesting to consider the extension of BIRD to strongly coupled systems. In such systems the scalar coupling between the protons is comparable in magnitude to the difference in chemical shifts between them. The Hamiltonian describing the scalar interaction between such spins takes the form

$$\mathcal{H}_{II}^J = \sum_{i < j} J'_{ij} I_{\nu_i} \cdot I_{\nu_j} \quad (6)$$

This term cannot be inverted with a single bilinear π rotation. In fact, a minimum of four bilinear π rotations, with appropriate phase shifts of the r.f. irradiation, is required for decoupling. This is illustrated in Figure 3(b), which indicates both the pulse train involved and the toggling frame value of the quantity $I_{\nu_i} \cdot I_{\nu_k} = I_{x_i} I_{x_k} + I_{y_i} I_{y_k} + I_{z_i} I_{z_k}$ in the windows between bilinear rotations. The notation used is that

$$I_{x_i} I_{x_k} \equiv XX \text{ and cyclic permutations.} \quad (7)$$

The average Hamiltonian for these windows is found by summing:

$$\begin{aligned} \bar{\mathcal{H}}^{(0)} \propto & (XX + YY + ZZ) + (-XX + YY - ZZ) + (-XX - YY + ZZ) \\ & + (XX - YY - ZZ) = 0. \quad (8) \end{aligned}$$

The chemical shifts of the satellite protons are preserved and spin-spin couplings eliminated to this order of approximation.

CONCLUSIONS

For weakly coupled systems BIRD has the advantage over decoupling by spin tickling of being broad band. An advantage over J- δ spectroscopy in some circumstances would be that it is accomplished in a single time dimension in real time rather

than requiring accumulation and manipulation of signal in two dimensions. A disadvantage is that it is only sensitive to those protons bound in magnetically equivalent groups to a ^{13}C . This lowers the available magnetization at natural abundance and means that protons in other binding environments do not appear in the BIRD chemical shift spectrum. Those lines which do appear are at the isotopically shifted values. The method's unique value will be in strongly coupled systems, where the other techniques are inapplicable.

ACKNOWLEDGEMENTS

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Figure Captions

Figure 1: Proton NMR spectra at 182 MHz of ethanol illustrating removal of J-couplings by BIRD. Samples were spun horizontally at 60-80 Hz in a vertical superconducting magnet with a horizontal solenoid r.f. coil. The linewidths are dominated by residual magnet inhomogeneity.

- (a) Normal spectrum of the methyl and methylene protons of unenriched ethanol in CHCl_3 (1:2 v/v).
- (b) ^{13}C satellite of [$\alpha\text{-}^{13}\text{C}$] ethanol and [$\beta\text{-}^{13}\text{C}$] ethanol in CHCl_3 (1:1:4 by volume, 90% isotopic purity at the labeled position). Suppression of magnetization from non- ^{13}C -bonded (non-satellite) protons was achieved by the method of ref. 13.
- (c) BIRD spectrum of the ^{13}C enriched sample used in (b) acquired using the pulse sequence of Fig. 3(a). Non-satellite magnetization has again been suppressed. All multiplet structure has collapsed, yielding singlet lines at the respective chemical shifts of the methyl and methylene groups.

Figure 2: Bilinear rotation pulse sequences. Strong proton $\pi/2$ pulses and periods of free evolution combine to produce propagators of the form $U(t) = \exp(-iJ_{IS}^p I_{S_z} t)$ where $p = x, y$; $J_{IS}^p = 2\pi J_{IS}$. These correspond to rotation about the proton p-axis, with the nutation angle given by the product $(1/2)J_{IS}^p t$. Strong π pulses on both spin species serve to remove Zeeman terms from the effective propagators for the sequences.

- (a) Simple bilinear rotation about the proton x-axis. Choosing $t = 4\tau = 1/J_{IS}$ results in a nutation angle of π .

- (b) Compensated bilinear rotation produced by alternate rotations about the proton x and y axes. For a π rotation, 4τ is chosen equal to $1/J_{IS}^0$ for some representative heteronuclear coupling J_{IS}^0 . This sequence is much less sensitive to the exact value of J_{IS} than is (a). This allows good bilinear π 's to be given to proton-carbon pairs with a range of couplings J_{IS} .

Figure 3: Pulse sequences for removal of J-couplings by BIRD. U_{π}^P represents a bilinear π rotation about the proton p-axis while Π_p^H represents a strong proton π pulse of phase p.

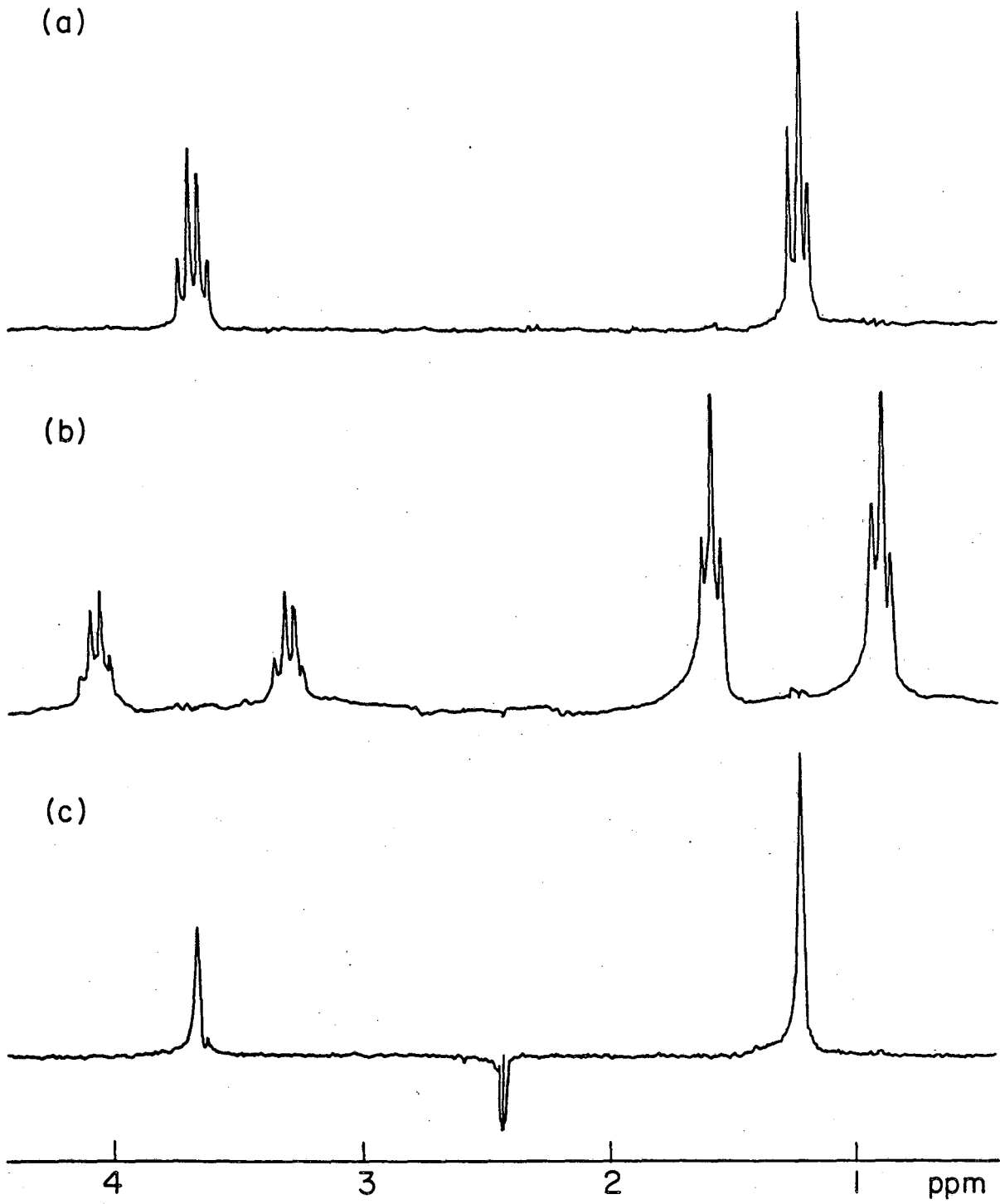
- (a) A single bilinear π /strong π combination is sufficient for decoupling a weakly coupled system. For the spectrum of Fig. 1(c) a compensated bilinear rotation (Fig. 2(b)) was used as U_{π}^X . A single point is sampled at the time t_1 and t_1 is incremented on successive shots. The initial 1H $\pi/2$ pulse was preceded by a second bilinear rotation sequence for suppression of non-satellite magnetization [13], as described in the text. Shown below the pulse sequence is the toggling frame value of the coupling $I_{zi} I_{zk}$ between satellite and non-satellite protons. The notation is $I_{pi} I_{pk} \equiv PP$, $P = X, Y, Z$.
- (b) A minimum of four bilinear π /strong π combinations are needed for decoupling strongly coupled systems. Shifts in the bilinear rotation axis are effected by shifting the phases of the proton pulses. The toggling frame value of the proton-proton coupling $(I_{\tau i} \cdot I_{\tau k})$ in the windows between rotations is shown below the pulse sequence. The average Hamiltonian, formed by summing these toggling frame values, is seen to be zero.

Figure 4: Schematic representations of BIRD using energy levels and magnetization vectors. A satellite proton is indicated by I, while I' represents a non-satellite proton. The sequence begins following a $\pi/2$ proton pulse with the proton spin vectors in the xy plane (1). Free evolution of the system for a time $t_1/2$ (2) causes precession of these vectors due to the chemical shift and heteronuclear coupling (3). A strong proton π pulse (4) rotates the magnetization vectors 180° about the pulse axis (5). For the I spin this also interchanges the identity of the spin vectors with respect to the ^{13}C . The bilinear π rotation (6), felt only by I, rotates that spin's magnetization vectors back, without interchanging their identities. Free evolution for an additional time $t_1/2$ (8) brings these two vectors back into line (9) with preservation of the I spin chemical shift (δ_{I}) and without broadening due to coupling to other protons. The I' spin chemical shift ($\delta_{\text{I}'}$) has been removed by this sequence; the final width of its spin vector reflects the preservation of coupling to other protons not explicitly included in the energy level diagrams.

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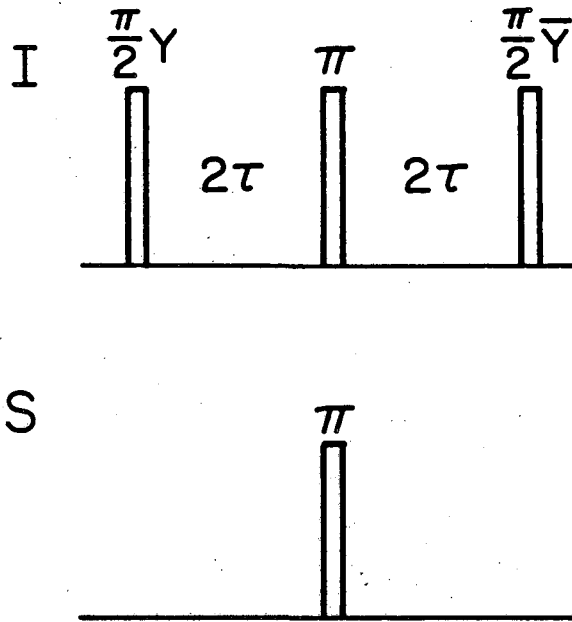
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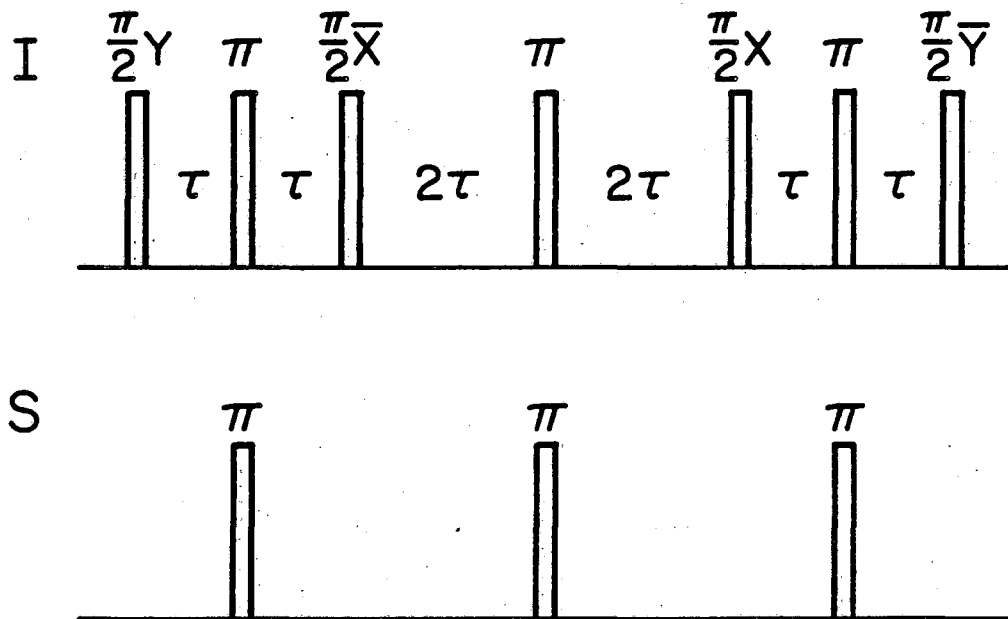
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Figure 1

(a)



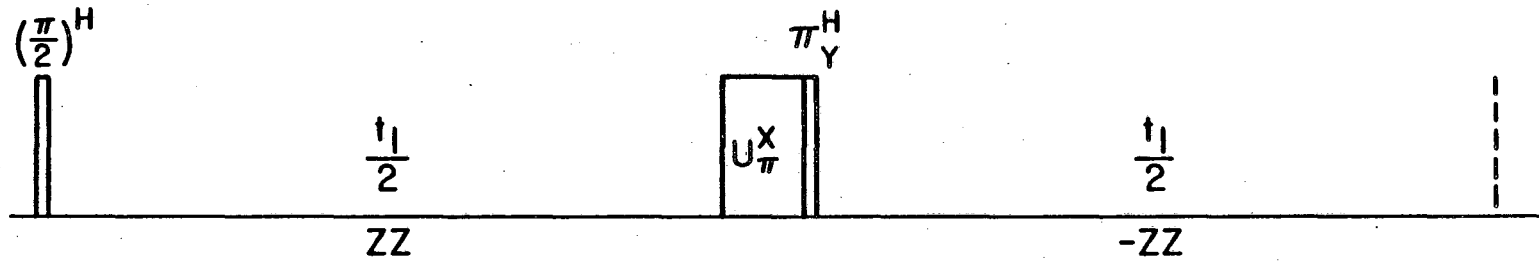
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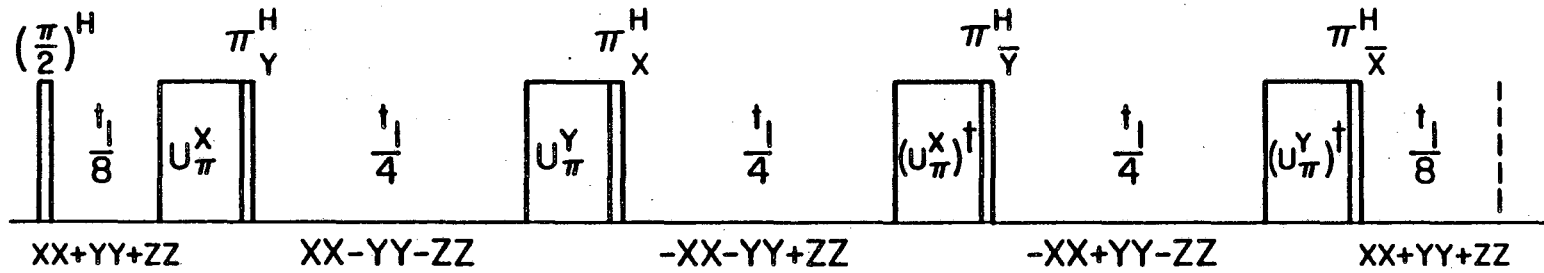
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Figure 2

(a)

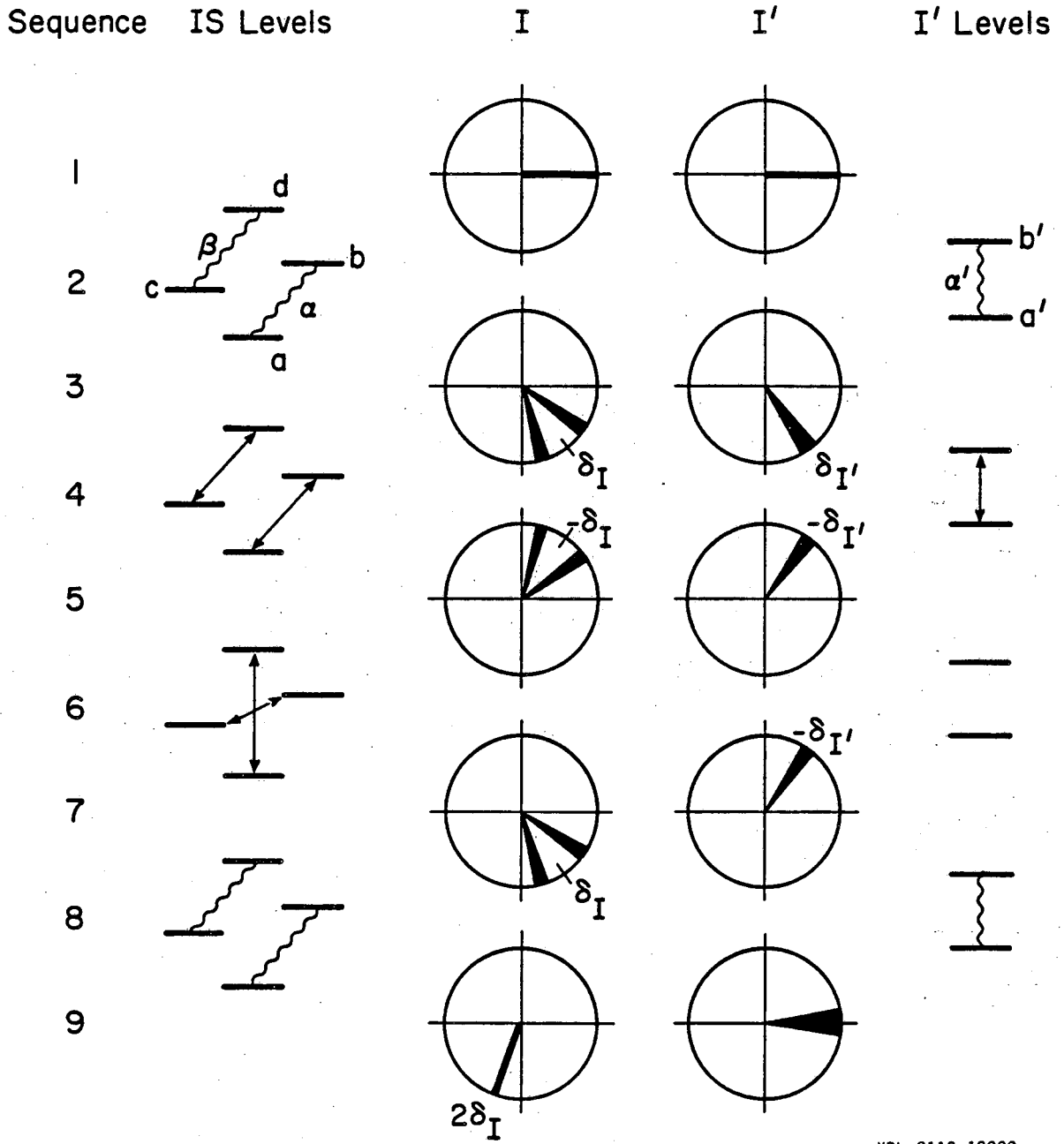


(b)



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Figure 3



XBL 8112-12909

Figure 4

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