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W.S. Warren and A. Pines

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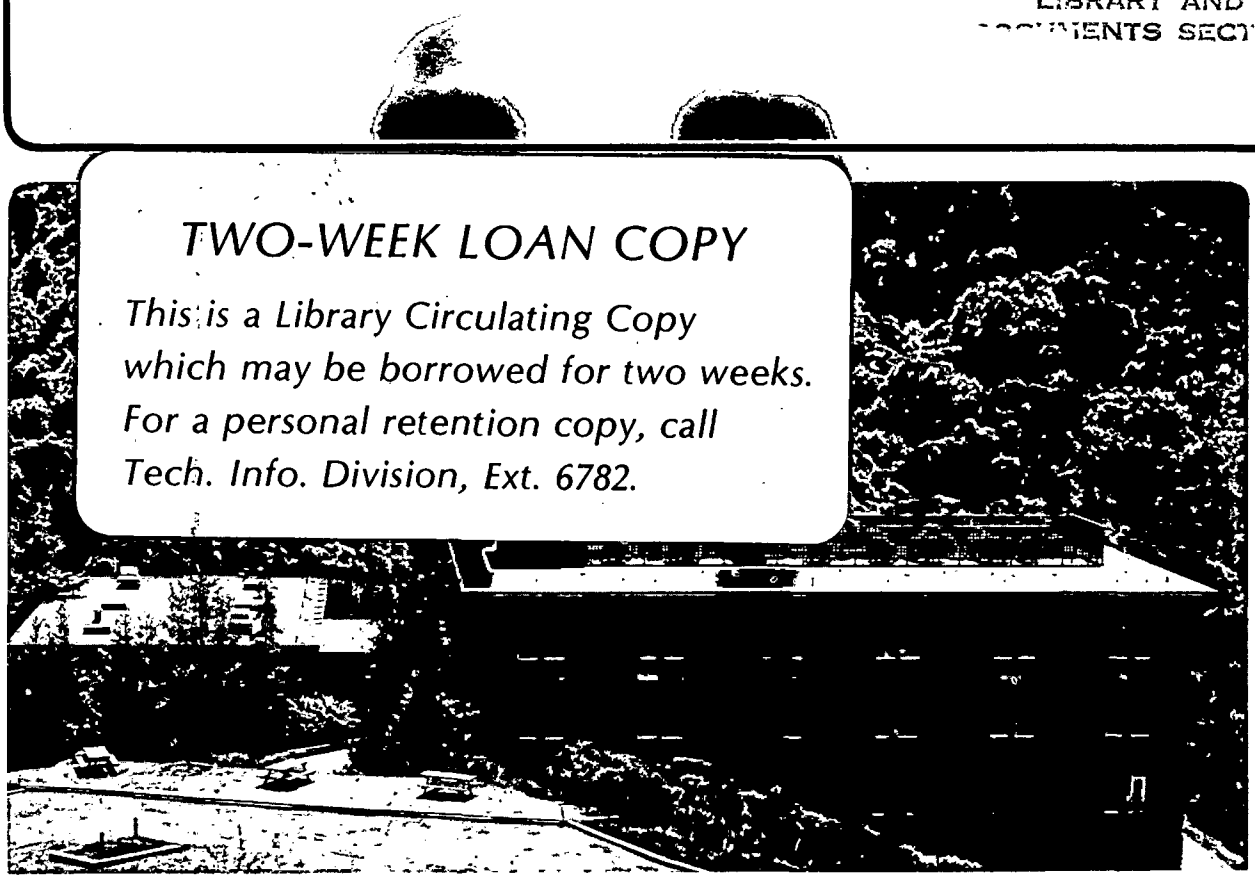

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W.S. Warren and A. Pines
Department of Chemistry and
Material and Molecular Research Division,
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Analogy of Multiple-Quantum NMR to Isotopic Spin Labeling

W. S. Warren and A. Pines*
Dept. of Chemistry and
Materials and Molecular Research Division, Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Abstract

The NMR of oriented molecules gives detailed structural information, but isotopic substitution is usually required for analysis. An alternative to synthesizing labeled molecules is to observe multiple-quantum spectra. Symmetry arguments show that multiple-quantum transitions yield similar information, and that the spectra can be predicted by analogy with labeling experiments. Several examples are shown to illustrate the versatility of this technique for determining molecular conformations and rates of intramolecular processes.

*Author to whom correspondence should be addressed.

Introduction

NMR spectroscopy of molecules dissolved in liquid crystal solvents has proven to be a powerful technique for determining molecular configurations and for studying intramolecular motion.[1] The liquid crystal causes a partial ordering of dissolved species so that the dipole-dipole coupling constants D_{ij} between each intramolecular pair of spins can be recovered from the spectrum. D_{ij} is proportional to $\langle (r_{ij})^{-3} \rangle$, so that, once all the lines of the spectrum have been assigned, the physical interpretation is straightforward. Unfortunately, the number of allowed transitions in the conventional NMR spectrum increases very rapidly as the number of like spins increases, and the spectrum of a large molecule is often unresolvable. As an example of this spectral complexity, consider the proton spectrum of oriented cyclooctatetraene, which is a fairly small molecule. The symmetry dictates that there are only six unique dipolar couplings, yet there are 2070 distinct transitions.[2] Clearly most of the lines give redundant information and these additional lines can make analysis impossible.

One approach to simiplifying spectra is isotopic substitution (for example, replacing protons with deuterons). This NMR version of a spin labeling experiment[3,4] is useful, since replacing most of the protons will reduce the number of possible transitions. Thus, one way to find the three coupling constants of oriented benzene, e.g., would be to synthesize the three different species which have only two protons; each of these species would have only one pair of lines in its deuterium decoupled spectrum. This approach has been extensively used to study large molecules,[1,2,5] but it has two important disadvantages: isotopic substitution may change the molecular configuration, the order parameters,[5] or the rate of internal processes, and synthesis of selectively labeled molecules is often difficult.

Pulse sequences have been designed which overcome the selection rule $\Delta M=1$ of normal NMR spectroscopy, thus permitting the observation of coherences between

states with arbitrary ΔM.[6-13] These multiple-quantum coherences can also be used to determine the dipole-dipole coupling constants. In addition, because the number of possibly distinct transitions falls off rapidly as M increases, multiple-quantum spectra do not require isotopic labeling to make them resolvable. In fact, in this paper we show that the observation of multiple-quantum transitions is a practical alternative to isotopic labeling, and that there is a great deal of similarity between these two techniques. Roughly speaking, the coherent flipping of n out of N spins inherently labels the (N-n) spins left behind. Thus, an alternative to synthesizing the three isomers of benzene-d_4 would be to look at the four-quantum spectrum of the fully protonated species: we will show later that the four-quantum spectrum contains exactly one pair of lines for each possible species, plus a highly degenerate central peak. Three pairs of lines give three coupling constants without any synthesis and without any possibility of isotopic distortions. Finally, we will work out several examples to show the wide range of molecules that can be analyzed by multiple-quantum techniques.

Determination of Multiple-Quantum Spectra

The NMR Hamiltonian for the N spins-1/2 of an oriented molecule can be written in the rotating frame (in units of $\hbar=1$) as

$$H = \left(\sum_{i>j} D_{ij}(3I_{zi}I_{zj}-\vec{I}_i\cdot\vec{I}_j) + J_{ij}(\vec{I}_i\cdot\vec{I}_j)\right) + \Delta\omega I_z. \tag{1}$$

The first term in equation (1) contains the direct and indirect spin-spin couplings, and the second term reflects any resonance offset. Other interactions, such as chemical shifts or heteronuclear couplings, will generally provide small corrections to this Hamiltonian. However, these additional interactions are usually suppressed in the experiments we will consider, so we will not discuss them here. If only the second term of equation (1) were present, the 2^N spin energy levels would be divided into small manifolds according to their total I_z

quantum number M, with the degeneracy of each manifold given by a binomial distribution. The first term in equation (1) breaks this degeneracy, so that, in the absence of any molecular symmetry, all eigenstates are nondegenerate. This distribution is shown schematically in figure (1). If N is large, there are many allowed single-quantum transitions (transitions between adjacent manifolds) and the lack of degeneracy in the eigenstates also makes the transitions non-degenerate, so the spectrum is complicated.

Single-quantum transitions can be observed after a single 90° pulse on a system with an initial spin density matrix proportional to I_z (figure 2(a)). After the pulse, the density matrix is proportional to I_x which is purely a single-quantum operator; $\langle I_x \rangle$ and $\langle I_y \rangle$, which are also single-quantum operators, are detected. Multiple-quantum transitions must be prepared and detected by a more complicated sequence, such as the sequence in figure 2(b).[6,7,10,13] Spin-spin interactions act on the system during the time τ to produce irreducible tensor operators of arbitrarily high rank, but these operators are still single-quantum since only tensor components of ± 1 are present. The second pulse produces multiple-quantum operators with arbitrarily high ΔM, as long as τ is comparable to or greater than the reciprocal of the single-quantum spectral width. These multiple-quantum operators evolve during t_1. The third pulse returns some of the multiple-quantum coherences to single-quantum coherences, which are detected after a time t_2. The sequence is repeated with different values of t_1 to create a multiple-quantum free induction decay, which is Fourier transformed to produce a spectrum. This pulse sequence generally produces transitions corresponding to all possible values of ΔM. Other sequences can create an artificial separation of the different values of ΔM (thus permitting the use of spin echoes to eliminate static inhomogeneity)[7,8] or can selectively excite only a few different values of ΔM,[13] or do both.

Simplicity of High Multiple-Quantum (ΔM = N, N-1, N-2) Spectra

The major advantage of observing multiple-quantum transitions is that the spectra corresponding to large values of ΔM are readily interpreted. For example, there is only one transition with $\Delta M=N$, because there is only one state with $M=N/2$ (all spins α) and only one state with $M=-N/2$ (all spins β). The spin-spin coupling in bilinear, so the dipolar energies of these two states are identical, and the transition frequency is $N\Delta\omega$. Therefore, the N-quantum transition gives the resonance offset (or, if chemical shifts are present, the sum of all the shifts) directly. In a typical nonselective experiment, the average transition intensity does not decrease as ΔM increases.[14] However, some individual transitions may be weak, just as in the normal single-quantum experiment.

Of course, the frequency of a single transition contains very little information about complicated molecules. The (N-1)-quantum and (N-2)-quantum spectra are still far simpler than the single-quantum spectrum, but contain enough transitions to be useful. There are N states with $M=\pm((N/2)-1)$, and $(N^2-N)/2$ states with $M=\pm((N/2)-2)$. The number of allowed transitions involving these states depends on the symmetry of the Hamiltonian. Even if the molecule has no symmetry, the dipolar Hamiltonian is bilinear, and is unaffected by flipping all spins. In this case the (N-1)-quantum spectrum has N pairs of lines ($M=(N/2)-1 \rightarrow M=N/2$, or $M=N/2 \rightarrow M=-((N/2)-1)$), and is symmetric about $(N-1)\Delta\omega$. This spectrum is similar to the single-quantum spectrum that could be produced if all of the molecules were cooled down into the ground state.[15] The (N-2)-quantum spectrum is also symmetric, and has N(N-1) pairs of lines ($M=N/2 \rightarrow M=-((N/2)-2)$, $M=(N/2)-1 \rightarrow M=-((N/2)-1)$, or $M=(N/2)-2 \rightarrow M=-N/2$) plus a highly degenerate peak at $(N-2)\Delta\omega$, arising from transitions between any $M=N/2-1$ eigenstate and the $M=-((N/2)-1)$ eigenstate generated by flipping all the spins. There are N(N-1) possibly different direct and indirect couplings, so roughly

this many pairs of lines are needed for complete characterization. Typically, each transition would be a few Hz wide, out of a total spectral width of many KHz. Therefore, the (N-1)-quantum and (N-2)-quantum transitions are usually resolvable, and assignment of these two spectra is sufficient to determine all dipolar couplings.

If the Hamiltonian has additional symmetry operations on a NMR time scale, the number of transitions decreases, because the eigenstates can be assigned to several irreducible representations (figure 3). Since the multiple-quantum spectra contain few lines to begin with, symmetry effects are easily noticed. The number of transitions can be determined by generating symmetry adapted states and this has been done for general isotropic systems.[12] However, for anisotropic systems this process can be quite involved. If only the number of transitions is required, simpler symmetry arguments will suffice.

Symmetry Considerations and Analogy to Isotopic Spin Labeling

Consider first the (N-1)-quantum spectrum. The states with M=N/2 (all spins α) and M=-N/2 (all spins β) are invariant to all molecular symmetry operations, hence they belong to the totally symmetric representation A_1. Therefore, the (N-1)-quantum transitions all have A_1 symmetry, and each A_1 eigenstate for M=(N/2)-1 will generate one transition, as will each A_1 eigenstate for M=-((N/2)-1). There is no symmetry reason for any of these transitions to be degenerate. In the spin product (SP) basis set, the states with M=((N/2)-1) are the N states with (N-1) spins α, and the remaining spin β; the opposite is true for M=-((N/2)-1). A_1 symmetry adapted states can be generated from this basis set by taking one SP state and applying all the symmetry operations of the spin system to it.[16] If this process is repeated for all the SP states, all the A_1 states are generated.

The symmetry operations of the spin system can be described from two different perspectives. Symmetry operations such as planes or axes of rotation can be

defined, and eigenstates can be classified according to their behavior under these symmetry operations.[16] A more versatile approach, which we will use here, is to describe symmetry operations by allowed permutations of the nuclei.[17,18] Two nuclei a and b are magnetically equivalent if there is a symmetry operation which turns a into b; this same symmetry operation need not convert b into a. If no such operation exists, the nuclei are inequivalent. Since each state in the SP basis for $M=\pm((N/2)-1)$ can be described by its single different spin, this definition implies that the number of A_1 symmetry adapted states will be equal to the number of inequivalent spins. Thus, each inequivalent spin produces one pair of (N-1)-quantum lines.

Spin product states are more easily visualized than are symmetry adapted eigenstates, and therefore it is convenient to work in this basis. It can be shown readily that the number of distinct n-quantum transitions can be determined from any convenient basis set (not necessarily the eigenbasis) by counting the number of n-quantum matrix elements which can evolve independently. Therefore, the number of transitions (but not the transition frequencies) can be determined in the spin product basis. In this basis, an (N-1)-quantum matrix element corresponds to flipping (N-1) spins in the local field of one spin which is left behind. This process inherently "labels" the remaining spin; it is still a proton, but it is distinguishable from all the other spins. The spin can be either α or β, so we expect one pair of lines for each inequivalent spin; if two spins are equivalent, there is a symmetry element which forces the two corresponding (N-1)-quantum matrix elements to be equal. The number of inequivalent spins is equal to the number of possible monosubstituted species, so we assign one pair of lines to each of those species.

The number of (N-2)-quantum transitions can also be easily determined in the SP basis set, and symmetry arguments show that the following counting scheme is correct. There are two fundamentally different ways to generate an (N-2)-quantum transition in the SP basis set. One way to generate an (N-2)-quantum

transition is to flip all N spins, starting from a state with one spin β and the rest α; therefore, these transitions correspond to $M=(N/2)-1 \rightarrow M=-((N/2)-1)$. Since all the spins flip, these N transitions have no dipolar energy, so they all occur at $(N-2)\Delta\omega$. A (N-2)-quantum transition can also be generated by flipping (N-2) spins in the local field of the remaining two, which we label x and y. The number of distinguishable ways in which two spins can be chosen out of N is determined by the symmetry of the molecule. It is equal to the number of different species with (N-2) isotopic labels. The two remaining spins may be $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, or $\beta\beta$, which gives a quartet if there is no symmetry element $x \rightarrow y$, $y \rightarrow x$, and a triplet if there is such a symmetry element (because then $\alpha\beta$ and $\beta\alpha$ are equivalent). Therefore, each unique <u>ordered</u> pair (xy) of spins in the molecule gives one pair of lines; in addition, there is always a highly degenerate peak at $(N-2)\Delta\omega$.

(N-3)-quantum transitions and lower orders can also be counted by similar schemes. However, the arguments above show that there is always at least one pair of lines in the (N-2)-quantum spectrum for each unique direct coupling constant, so the (N-3)-quantum spectrum mainly provides redundant structural information. In addition, the effectsof intramolecular motion, if they can be detected at all by NMR, can be detected in the (N-1)- or (N-2)-quantum spectra. Any process which causes exchange or pseudoexchange (rotation about a bond, for example) between inequivalent sites would decrease the number of possible monosubstituted species, and therefore would affect the (N-1)-quantum spectrum. If only magnetically equivalent sites are involved, the motion operator commutes with the Hamiltonian in equation (1) unless the ordered pair of spins (ij) is transformed into an inequivalent ordered pair (kl). Since this process would decrease the number of possible disubstituted species, it affects the (N-2)-quantum spectrum. The main advantage of assigning transitions in the (N-3)-quantum spectra or lower-quantum spectra is that the additional line assignments give coupling constants with better accuracy.

Examples of Multiple-Quantum Spectra and the Isotopic Labeling Analogy

In this section we show how multiple-quantum NMR can be applied to specific molecules, and we illustrate the use of the isotopic labeling analogy. The number of (N-1)-quantum pairs will always be equal to the number of different species with all but one of the proton removed. Each possible species with all but two protons removed contributes either a triplet or a quartet to the (N-2)-quantum spectrum. If we label the two remaining protons x and y, and if there is a symmetry element which exchanges x and y, a triplet results; if there is no such element, a quartet (two pairs) results, as mentioned earlier. Thus, we can assign one pair of lines to each different way that one proton can be labeled x, and another proton y. This scheme is used in all the examples that follow.

Acetonitrile (A_3, with C_{3v} symmetry)

The acetonitrile molecule (CH_3CN) contains only three protons, so its single-quantum spectrum is easily resolvable. However, the multiple-quantum spectra are useful in studying the relaxation of an oriented methyl group.[19] An unsymmetrical three-spin system would have one three-quantum transitions, six two-quantum transitions, and fifteen one-quantum transitions (three of these are degenerate and six others are weak if chemical shift differences are small) because there are three eigenstates each for $M=\pm 1/2$ and one eigenstate each for $M=\pm 3/2$. The high symmetry of a methyl group reduces the number of transitions considerably, as shown in figure 4. There is only one pair of two-quantum transitions, since there is only one monoprotonated species CD_2HCN; the position of the proton is labeled x in the figure. Similarly, there is only one diprotonated species CDH_2CN, and this gives a triplet in the one-quantum spectrum, because there is a symmetry operation which exchanges the two protons. This can be seen by labeling the two protons k and y, as in the figure, and noting that the two ways to do this are related by a mirror plane. The three protons are magnetically

fully equivalent (each spin is coupled identically to every other spin), so the indirect spin-spin coupling is unobservable. The single direct spin-spin coupling can be extracted from the one-quantum or the two-quantum spectrum.

Benzene ($AA'A''A'''A''''A'''''$, with C_{6v} symmetry)

The single-quantum spectrum of a six-spin system without symmetry would have 792 transitions, but only 15 different coupling constants. The C_{6v} symmetry of benzene reduces the number of single-quantum transitions to 76 and the number of different couplings to three.[20] All the spins are magnetically equivalent, but they are not magnetically fully equivalent because there is more than one coupling; this makes the spectroscopic notation $AA'A''A'''A''''A'''''$ in anisotropic solvents, as opposed to A_6 in isotropic solvents.

The high symmetry also reduces the number of allowed multiple-quantum transitions,[6,7] as shown in figure 5. There is only one species of monoprotonated benzene ($C_6D_5H_1$) so the five-quantum spectrum has one pair of lines, instead of the six pairs expected for an unsymmetrical molecule. There are only three possible diprotonated benzenes ($C_6D_4H_2$), corresponding to the ortho, meta, and para configurations, so the four-quantum spectrum consists of three triplets, for a total of seven lines, instead of the 61 four-quantum lines found for an unsymmetrical six-spin molecule. The experimental spectra verify these predictions, and therefore are consistent with the assumed geometry.

It is useful to consider how the spectra would change if distortions were present on an NMR time scale. Most distortions, such as an elongation along an axis perpendicular to the C_6 axis, would make the spins inequivalent and therefore would create more five-quantum and more four-quantum transitions. However, if the bonds alternated between two different lengths, as in the classical nonresonant structure with three double bonds, all the spins would remain equivalent, and the five-quantum spectrum would still have only one pair of lines. In this case more lines would be added to the four-quantum spectrum. However, the extra lines

might be expected to be weak if distortions are small, and would not be produced at all if the distortions were rapid (which they certainly are in this system).[21]

Maleic Anhydride (A_3A_3' with uncorrelated methyl group motion)

At room temperature the two methyl groups of this molecule are expected to rotate rapidly. As a result, all six spins are equivalent. There is only one possible monoprontonated species, so there is only one pair of five-quantum lines, as shown in figure 6. However, the equivalence of the spins reveals nothing about possible correlated motion between the two groups. Mutliple-quantum spectroscopy provides a particularly elegant test of correlation, because the number of lines in the four-quantum spectrum is affected. If the methyl group undergoes uncorrelated motion, there are only two possible diprotonated species, giving five lines; if the motions are correlated like two gears, there are three possible disubstituted species and seven lines. Recent studies[21] have shown that only five lines are present at room temperature, and that their positions are consistent with uncorrelated motion.

Cyclooctatetraene (COT) (AA'A''A'''A''''A'''''; symmetry depends on temperature)

Cyclooctatetraene, C_8H_8, has been shown to have D_{2d} symmetry at low temperatures by electron diffraction studies. With this tub-shaped symmetry, the single-quantum spectrum has 2070 transitions[2], as mentioned earlier. At room temperature, almost all of these transitions are broadened by a bond shift process, as shown in figure 7. This process can be viewed as a pseudorotation: spin 1 becomes spin 2, spin 2 becomes spin 3, and so forth. The transitions are not resolvable, so the bond shift process has been analyzed by isotopic substitution;[2] the spectra of a random mixture of all possible diprotonated species were analyzed.

Multiple-quantum spectroscopy allows the fully protonated species to be directly studied. Since all the spins are equivalent, there is only one monoprotonated species, independent of the bond shift rate; therefore there would be only one pair of seven-quantum lines, and these lines give no kinetic information.

However, the six-quantum spectrum is affected by the bond shift. At low temperatures the D_{2d} symmetry should give six independent dipolar coupling constants (D_{12}, D_{13}, D_{14}, D_{15}, D_{16} and D_{18}; $D_{17}=D_{13}$ by symmetry), so there are six diprotonated species. The species (1,3) gives a quartet, since there is no symmetry operations $1 \rightarrow 3$, $3 \rightarrow 1$; all the other species give triplets. Labeling the two protons x and y as before, we find x=1, y=2; x=1, y=3; x=3, y=1 ($\equiv$x=2, y=4 by symmetry); x=1, y=4; x=1, y=5; x=1, y=6 ($\equiv$x=2, y=5 by symmetry); and x=1, y=8 ($\equiv$x=2, y=3 by symmetry), so there should be seven pairs of lines. At high temperature, the rapid bond shift makes x=1, y=2 equivalent to x=2, y=3; x=1, y=3 equivalent to x=2, y=4; and x=1, y=4 equivalent to x=2, y=5. The number of six-quantum pairs should therefore be reduced to four.

The effective permutation group is the same as that of a regular octagon; however, since $D_{ij} \sim \langle r_{ij}^{-3} \rangle$, the coupling constants will not have the ratios that octagonal symmetry would dictate. This molecule is currently being studied.

<u>Substituted Biphenyls</u> (AA'A''A'''BB'B''B'''; symmetry depends on model)

The relative motion of the two phenyl groups of biphenyl and its derivatives can be studied by measuring the direct coupling constants. However, the single-quantum spectrum of biphenyl is extremely complex. Some simplification can be achieved by removing the two protons on the ends of the molecule, since their distance is independent of the ring motion, but even with this substitution the single-quantum lines cannot be completely resolved. Diehl and co-workers[23] analyzed the spectrum of 4, 4'-dichlorobiphenyl by picking out a number of the transitions and iterating on their frequencies. The spectrum of 4, 4'-bipyridyl has also been analyzed.[24]

By contrast, the multiple-quantum spectra of substituted biphenyls are easily resolvable. The seven-quantum spectrum will always contain two pairs of lines of the substituents are identical, since there are two monoprotonated species, as shown in figure 8. Even if the substituents are not identical, the

biphenyl structure is not likely to be substantially distorted, so two pairs are still expected (although the lines may be split[25]). The number of six-quantum lines depends on the motional model. Either free rotation or jumps between four equivalent sites (corresponding to inter-ring angles θ, $-\theta$, $\pi + \theta$, and $\pi-\theta$) will give seven diprotonated species; labeling the spins x and y shows that there are ten pairs of lines. However, jumps between only two sites (corresponding to inter-ring angles θ and $-\theta$) will give fourteen pairs of lines, as will a small amplitude rocking motion around a single site. Eight pairs of lines are visible above the noise level in the six-quantum spectrum of 4-cyano-4'-pentyl-d_{11}-biphenyl,[25] and their positions coincide with those of eight of the ten pairs which a four-site model would generate. The remaining two pairs are expected to be weak, and extensive signal averaging would probably be required to observe them. It is interesting to note that isotopic labeling of the substituents was combined with multiple-quantum NMR to study this molecule. Synthesizing the molecule with a perdeuterated chain is straightforward[26] but selective substitution on the rings is more difficult.

Conclusion

We have presented symmetry arguments which allow prediction of the general features of the multiple-quantum spectra without having to explicitly diagonalize the Hamiltonian. The number of transitions is predicted by analogy with spin labeling, since the high multiple-quantum transitions can be viewed as inherently labeling most of the spins. We have given examples of the simplicity of (N-1)-quantum and (N-2)-quantum spectra. We believe that multiple-quantum spectroscopy, in combination with relatively simple isotopic substitutions when necessary (for example, perdeuterating a side chain), should be a useful future approach for studying complex molecules.

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FIGURE CAPTIONS

Figure 1. Schematic energy level diagram for a system of N spins-1/2 without symmetry. All the eigenstates can be nondegenerate, and there are many single-quantum transitions. However, there is only one N-quantum transition. There are only N pairs of (N-1)-quantum transitions, and N(N-1) pairs of (N-2)-quantum transitions, plus a central line.

Figure 2. Simple pulse sequences for NMR experiments. The sequence in Figure 2a prepares and detects only single-quantum transitions. The sequence in Figure 2b prepares and detects multiple-quantum transitions.

Figure 3. Schematic energy level diagram for a system of N spins-1/2 with symmetry. The states with $M=\pm N/2$ belong to the totally symmetric representation A_1, so all N-quantum or (N-1)-quantum transitions are in that representation. (N-2)-quantum transitions can come from other representations as well.

Figure 4. The multiple-quantum spectra of the methyl group of acetonitrile. The high symmetry allows for only one monoprotonated and one diprotonated species, so the two-quantum spectrum has one doublet, and the three-quantum spectrum has one triplet.

Figure 5. The multiple-quantum spectra of benzene. There is only one possible monoprotonated species, so there is one pair of five-quantum lines. The three diprotonated species imply three triplets (seven lines) in the four-quantum spectrum.

Figure 6. The multiple-quantum spectra of maleic anhydride. The two methyl groups would give three diprotonated species if their motion were correlated, but only two if not, so the number of four-quantum lines depends on the motional model. There is only one monoprotonated species, so the five-quantum spectrum does not reflect correlations.

Figure 7. The multiple-quantum spectra of cyclooctatetraene. The single-quantum spectrum has 2070 lines, and is totally unresolvable when the bond shift rate is comparable to dipolar couplings. The six-quantum transitions also broaden, but they are still resolvable. In the high temperature limit, six lines have disappeared since the number of diprotonated species is reduced. There is only one monoprotonated species at any temperature, so the seven-quantum spectrum is unaffected by the bond shifts.

Figure 8. The multiple-quantum spectra of a typical para-disubstituted biphenyl. The two substituents are different, but the rings should not be strongly distorted, and the dipolar Hamiltonian is assumed to have a symmetry operation which exchanges them. There are then two monoprotonated species, so there are two pairs of seven-quantum lines. Jumps between four equivalent values for the inter-ring angle would give seven diprotonated species (four triplets and three quartets) and ten pairs of lines.

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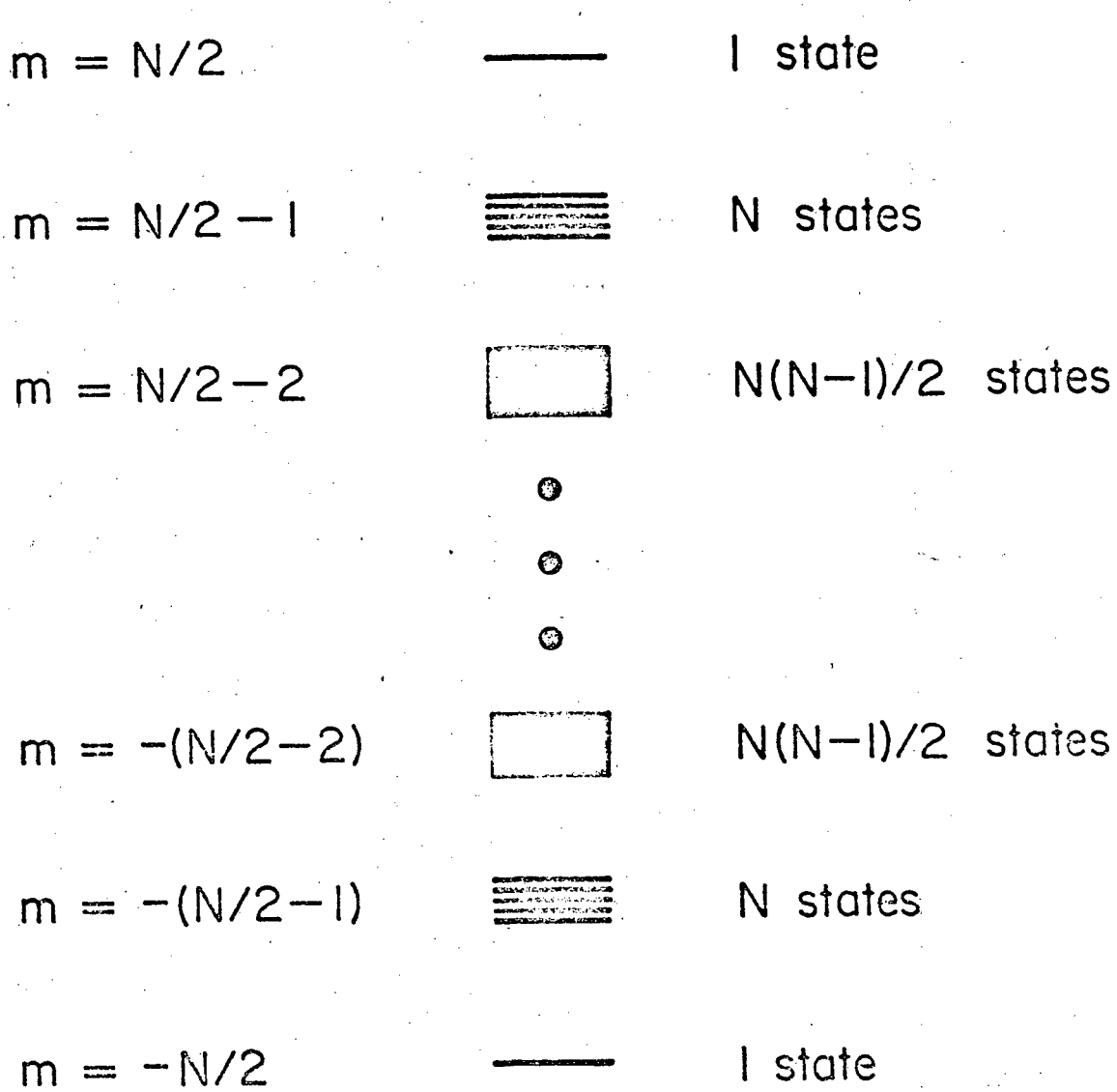
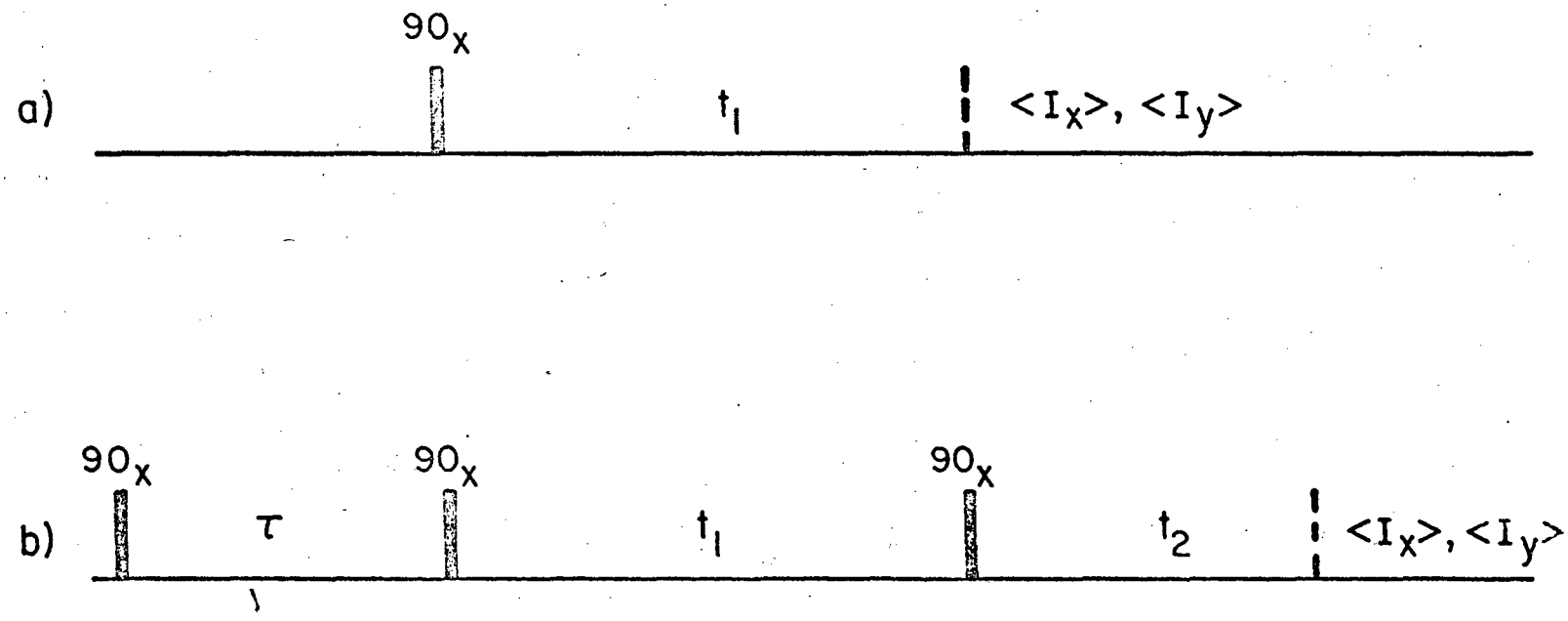
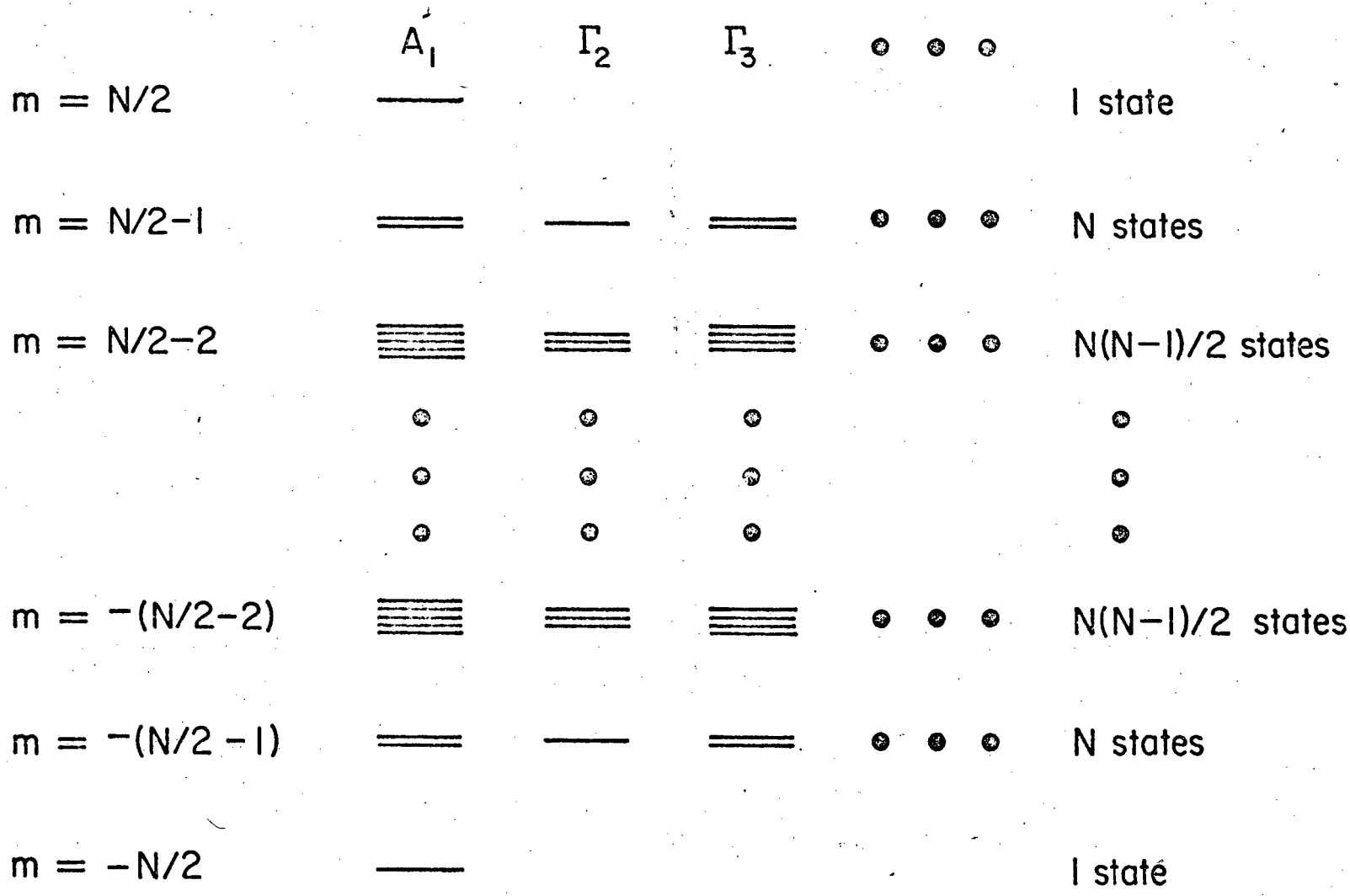

m = N/2
1 state
m = N/2 − 1
N states
m = N/2 − 2
N(N−1)/2 states
m = −(N/2−2)
N(N−1)/2 states
m = −(N/2−1)
N states
m = −N/2
1 state

XBL 805-9725



XBL 807-10631


A1
Γ2
Γ3
m = N/2
1 state
m = N/2−1
N states
m = N/2−2
N(N−1)/2 states
m = −(N/2−2)
N(N−1)/2 states
m = −(N/2 −1)
N states
m = −N/2
1 state

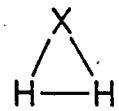
XBL 805-9541

n–Quantum Spectra (n=1,2,3)

Acetonitrile

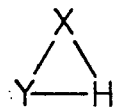
Three–quantum: one line

Two–quantum:

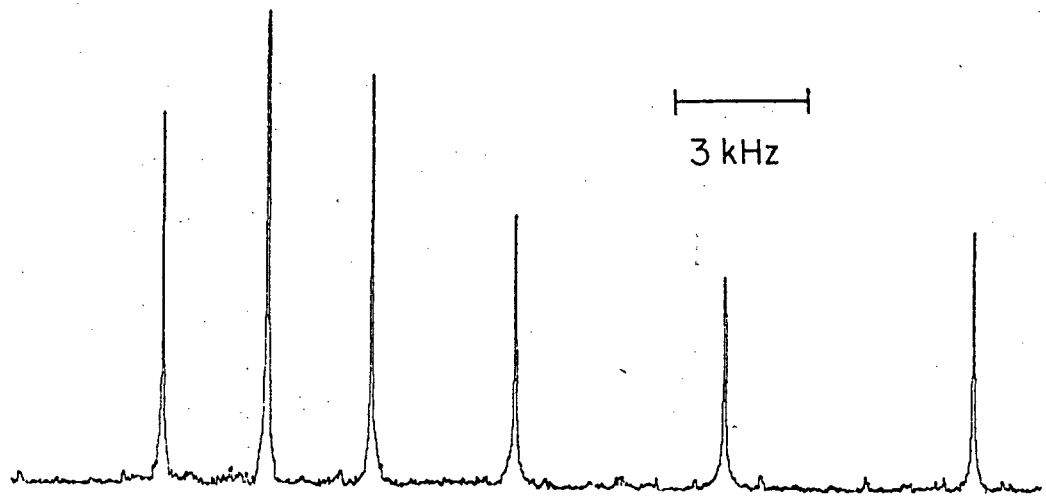


one pair

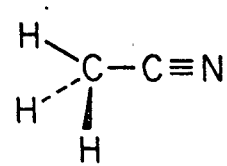
One–quantum:



one pair



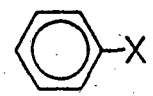
n = 1 n = 2 n = 3



XBL 807-10630

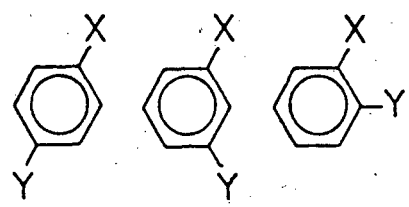
Six-quantum: one line

Five-quantum:



one pair

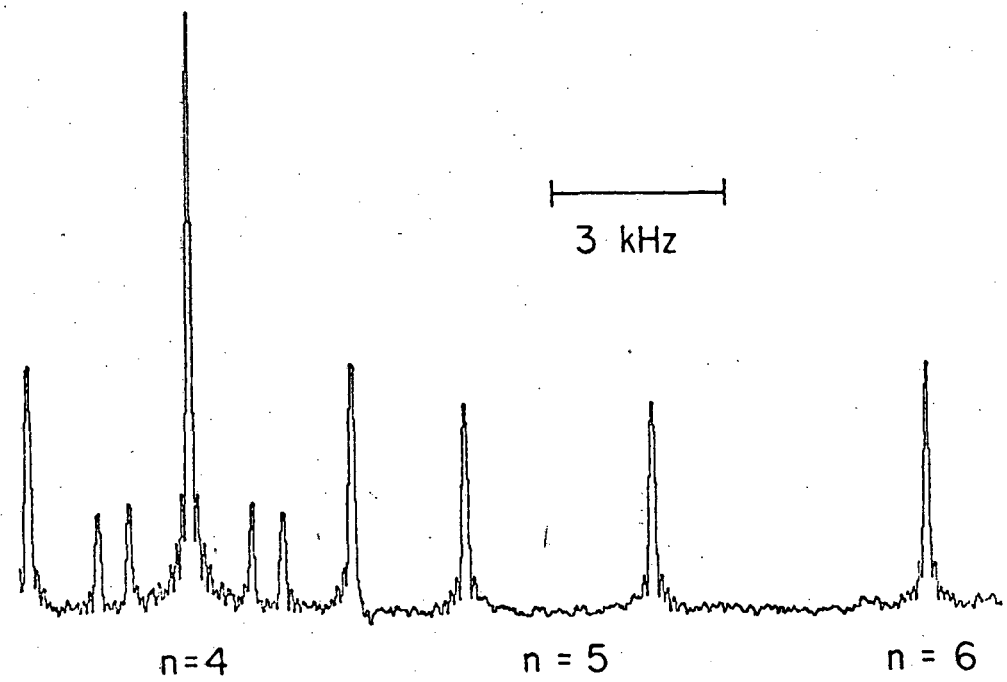
Four-quantum:

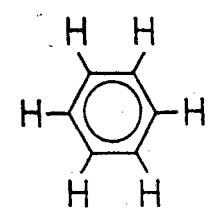


three pairs

n-Quantum Spectra (n = 4,5,6)

Benzene

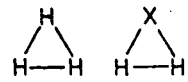




XBL 807-10629

Six–Quantum: one line

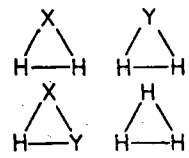
Five–Quantum:



one pair

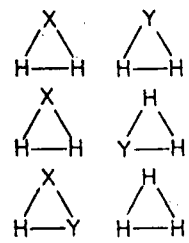
Four–Quantum:

uncorrelated motion



two pairs

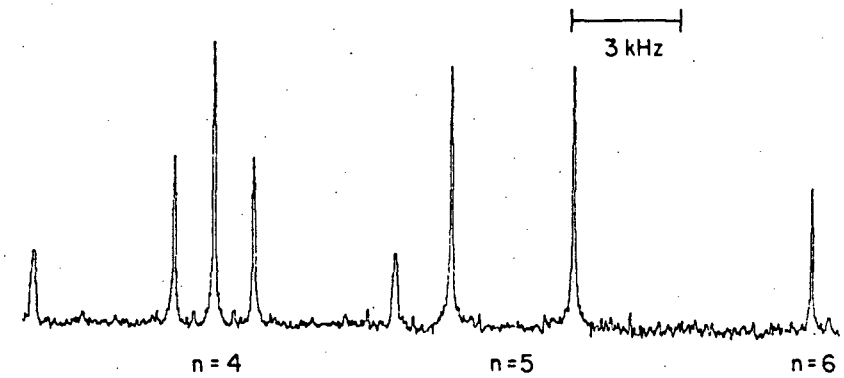
correlated motion

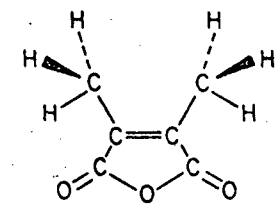


three pairs

n–Quantum Spectra (n = 4,5,6)

Maleic Anhydride

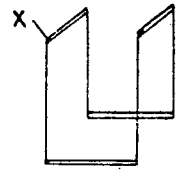




XBL 807-10632

Eight-Quantum: one line

Seven-Quantum:



one pair

Six-Quantum x=1, y=5

x=1, y=2 ⟷ x=2, y=3

x=1, y=3 ⟷ x=2, y=4

x=1, y=4 ⟷ x=2, y=5

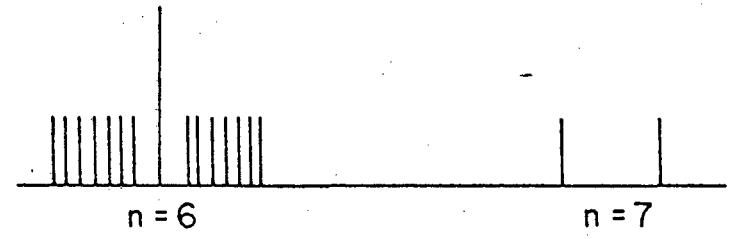
Slow bond shift: seven pairs

Fast bond shift: four pairs

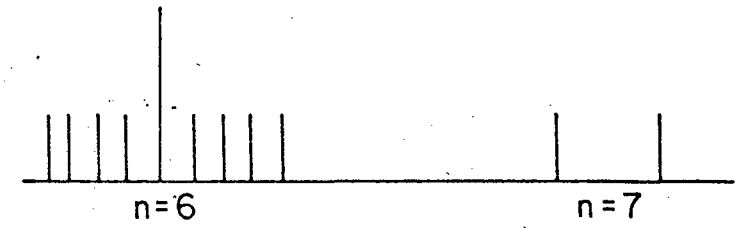
n-Quantum Predicted Spectra (n = 6,7)

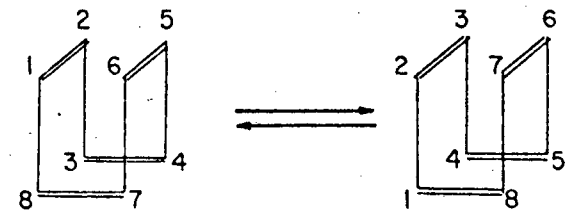
Cyclooctatetraene

Slow bond shift



Rapid bond shift



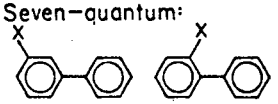


Note: Bond angles exaggerated

XBL 807-10633

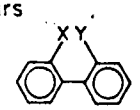
Eight-quantum: one line

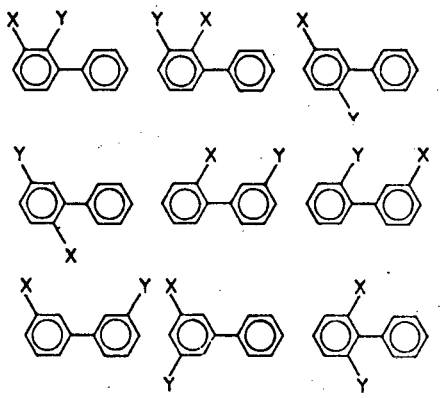
Seven-quantum:



two pairs

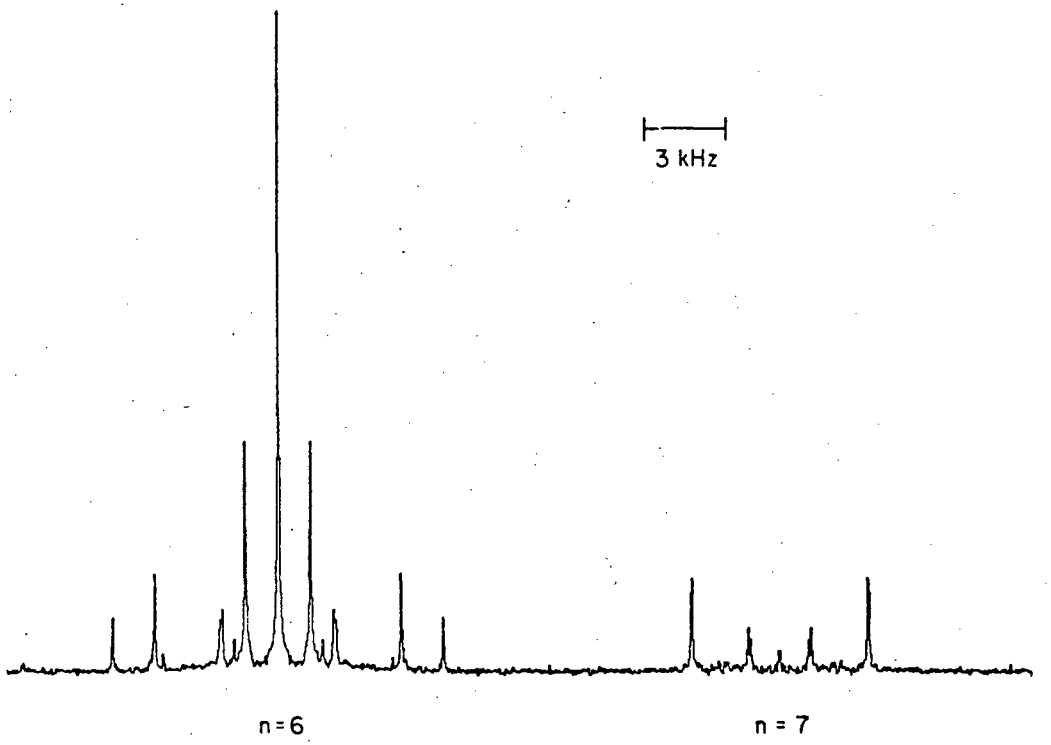
Six-quantum:

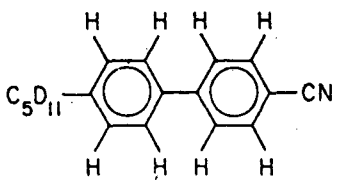




ten pairs

n-Quantum Spectra (n=6,7)
Substituted Biphenyl





XBL 807-10634

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