Multiplet Guide and Workbook

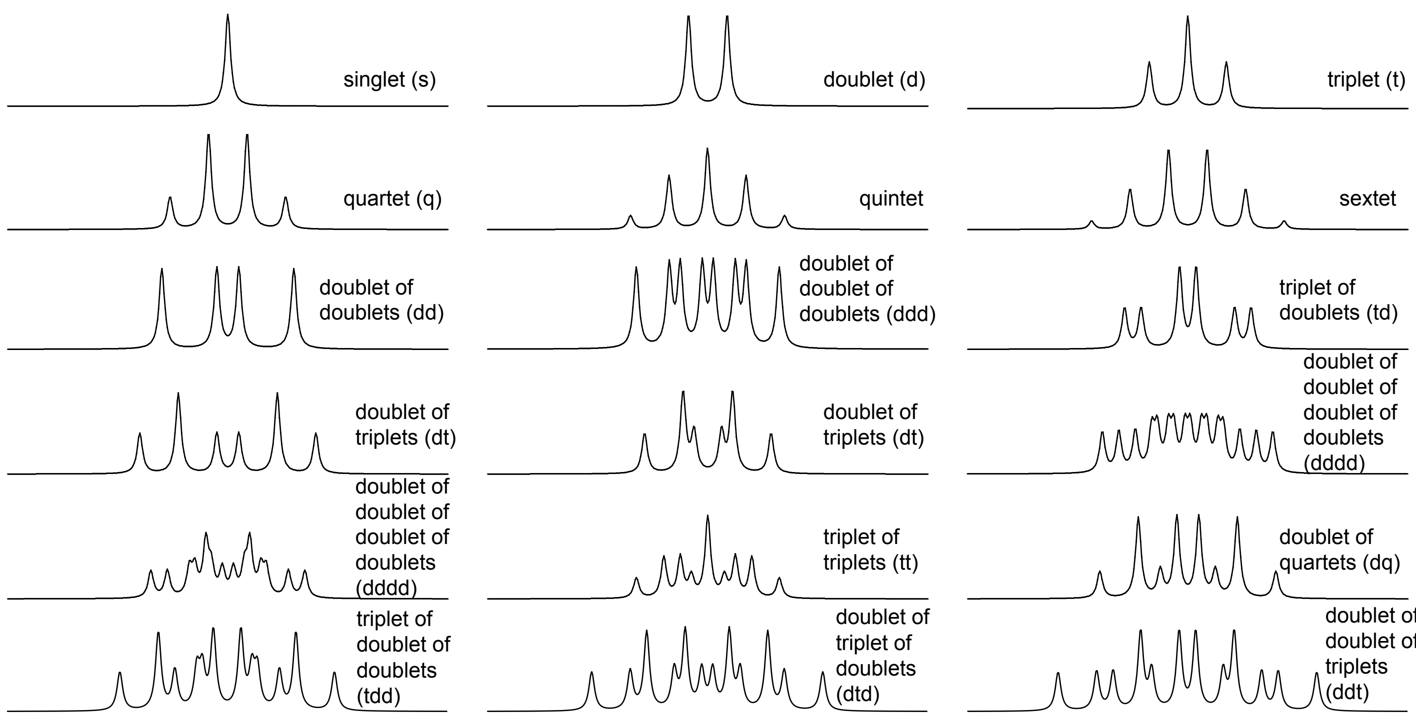
(J. Nowick)

There are a limited number of first-order multiplets that are typically encountered in ^{1}H NMR spectroscopy. In addition to the simple couplings involving equivalent coupling constants [doublet (d), triplet (t), quartet (q), quintet, sextet, septet, octet, and nonet], there are more complex patterns involving different coupling constants. Common patterns include the doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of doublets (ddd), and a few involving more than three couplings (dddd, dq, qd, tt, ddt, dtd, tdd, etc.). The following examples and problems are designed to help you better understand these couplings.

CONTENTS:

It should be noted that there are two conflicting systems of nomenclature that are in use. (Alas, I can show you authoritative sources supporting each system.) For the purposes of this course, we will name multiplets such that *the biggest coupling constant determines the "first name" of the multiplet and the smallest coupling constant determines the "last name."* In this system of nomenclature, a *doublet of triplets* (dt) is six-line pattern with one large coupling and two equal small couplings. It may be thought of as a "pair of triplets." Conversely, a *triplet of doublets* (td) is a six-line pattern with two equal large couplings and one small coupling. It may be thought of as a "trio of doublets in 1:2:1 ratio".

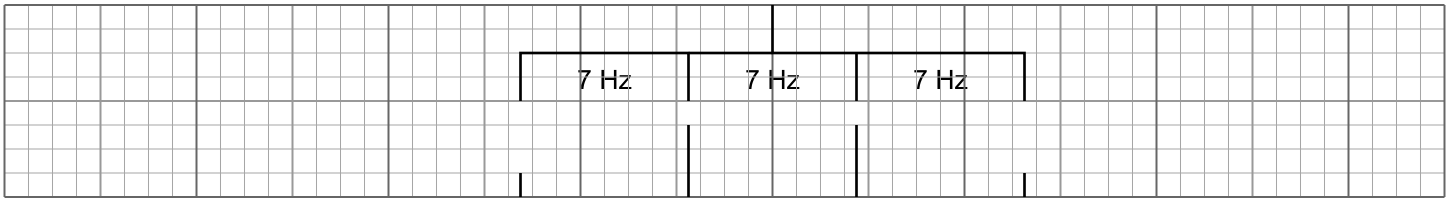
It should also be noted that the approach taken in this guide is based on pattern recognition and is complementary to the purely analytical approach described by Hoye and coworkers (*J. Org. Chem.* **1994**, *59*, 4096 and *J. Org. Chem.* **2002**, *67*, 4014). The analytical approach, although particularly powerful for the most complex splitting patterns (e.g., dddd), suffers the disadvantage that it tends to result in experimentally insignificant differences in coupling constants being determined (e.g., dddd, J = 3.6, 3.5, 3.3, 3.2 Hz vs. quintet, J = 3.4 Hz). It also does not perform well in complex multiplets in which lines cannot be resolved. For this reason, I prefer the pattern-recognition approach described herein.



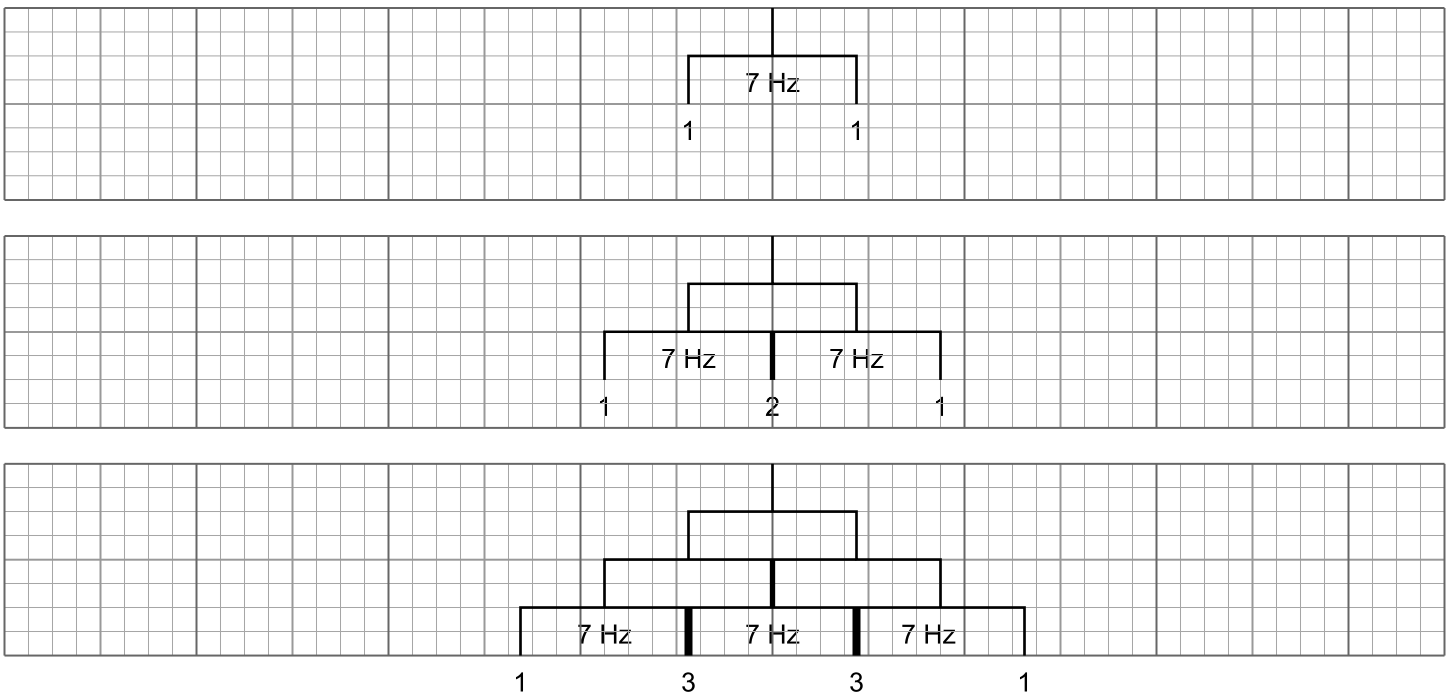
Quartet

Description: A quartet (q) is a pattern of evenly-spaced lines with 1:3:3:1 relative intensities (or close to 1:3:3:1 relative intensities) that are separated by the coupling constant *J*. The quartet arises from coupling with equal coupling constants to three protons (or other spin 1/2 nuclei).

Example: q, *J* = 7 Hz

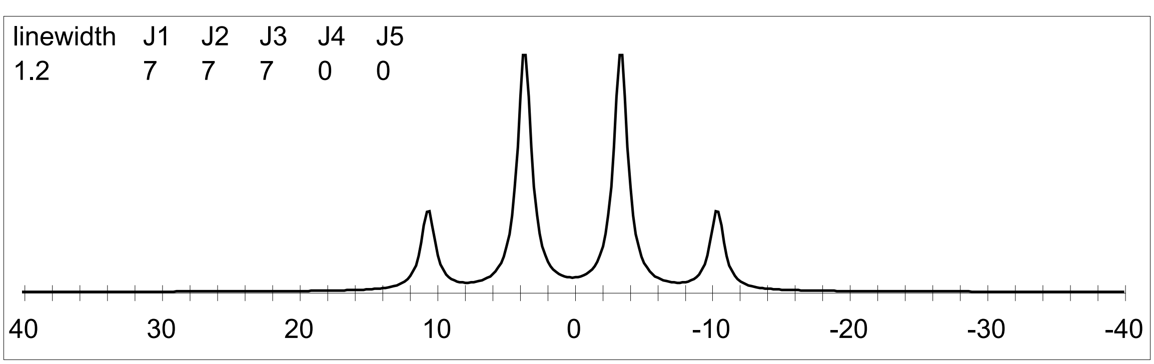


A quartet may be thought of as a doublet of doublet of doublets with three equal splittings and the following splitting tree, which has been represented as three successive drawings.



The *J* value of a quartet can always be determined by measuring the distances between individual lines. With real data, it is best to take the average distance between lines (which is also the distance between the first and last line divided by three).

Simulation of a quartet *J* = 7 Hz gives the familiar pattern:



Triplet

Description: A triplet (t) is (FINISH DESCRIPTION)

Example: t, J = 6 Hz (DRAW A SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

A triplet may be thought of as doublet of doublets with two equal splittings. (DRAW THE SPLITTING TREE AS TWO SUCCESSIVE DRAWINGS.)

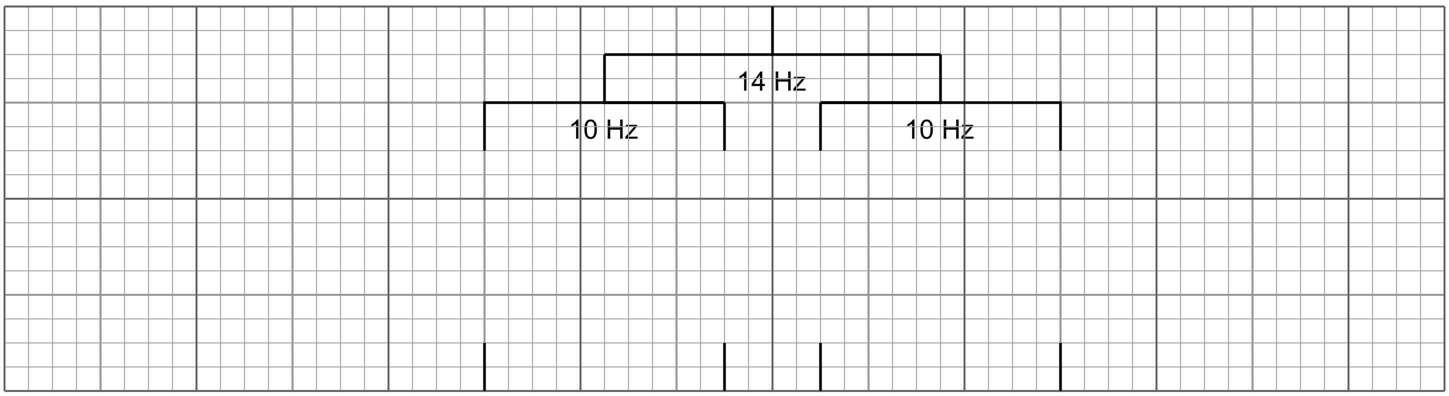
The J value of a triplet can always be determined by (FINISH THE DESCIPTION)

Simulation of a triplet J = 6 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

Doublet of Doublets

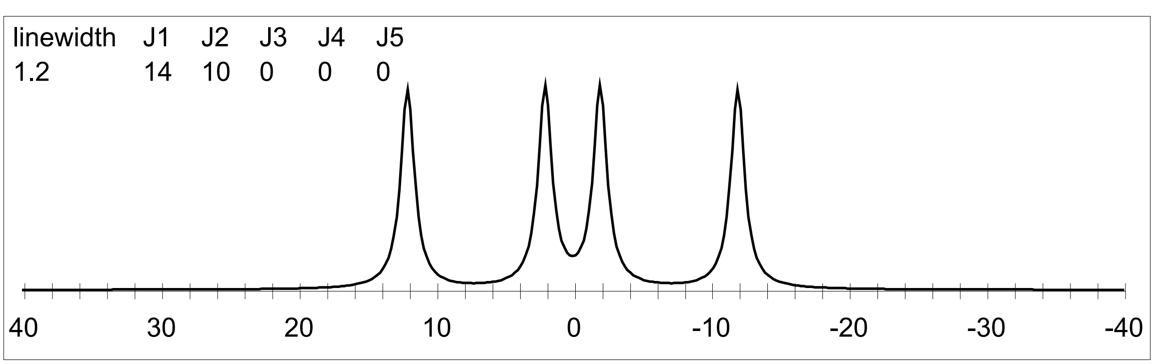
Description: A doublet of doublets (dd) is a pattern of up four lines that results from coupling to two protons (or other spin 1/2 nuclei). The lines are of all equal intensities (or close to equal intensities). If both of the coupling constants are the same, a triplet (t) occurs.

Example: dd, J = 14, 10 Hz



The smaller J value of a dd is always the distance between the first and second line (or the third and fourth line). The larger J value of a dd is the distance between the first and third line (or the second and fourth).

Simulation of a dd (J = 14, 10 Hz) gives a typical four-line pattern.

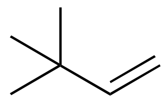


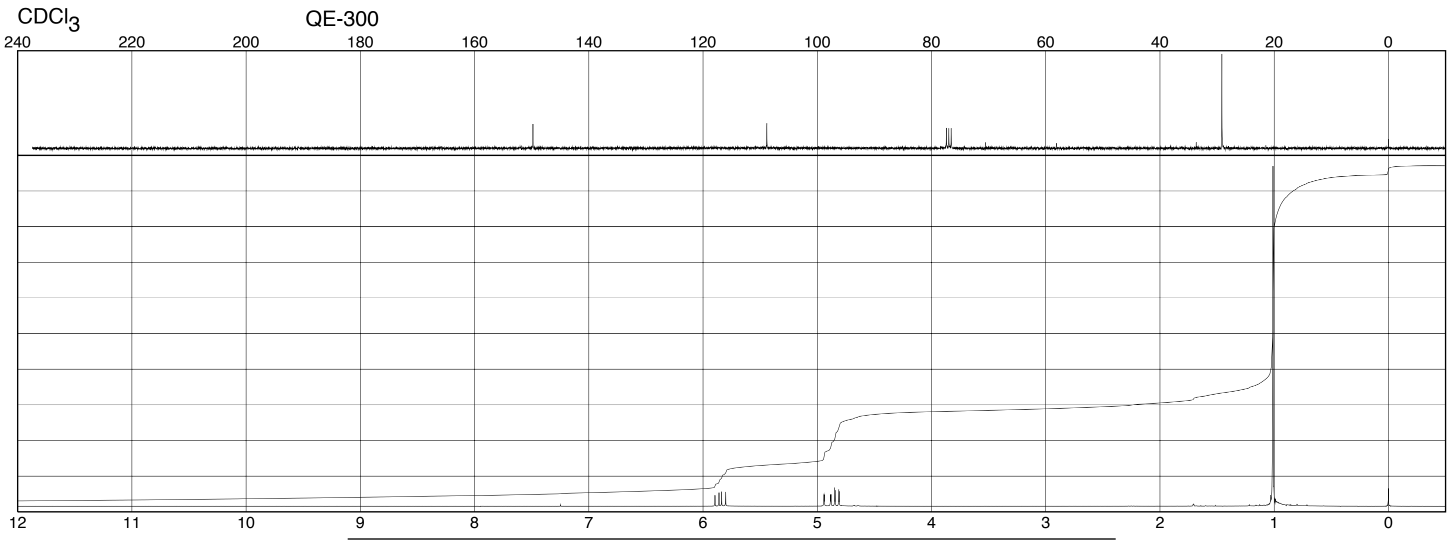
Doublet of Doublets (continued)

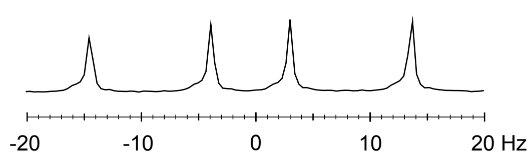
Example: dd, *J* = 14, 3 Hz (DRAW THE SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a dd *J* = 14, 3 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

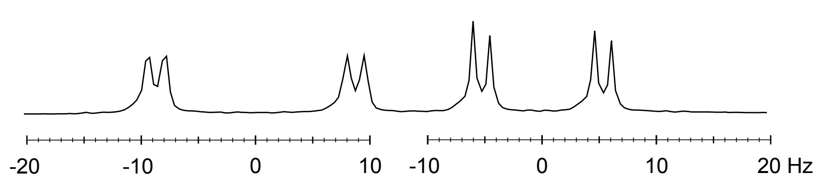
Doublet of Doublets Examples: 3,3-Dimethyl-1-butene







5.85 (dd, J = 17.5, 10.7 Hz, 1H)

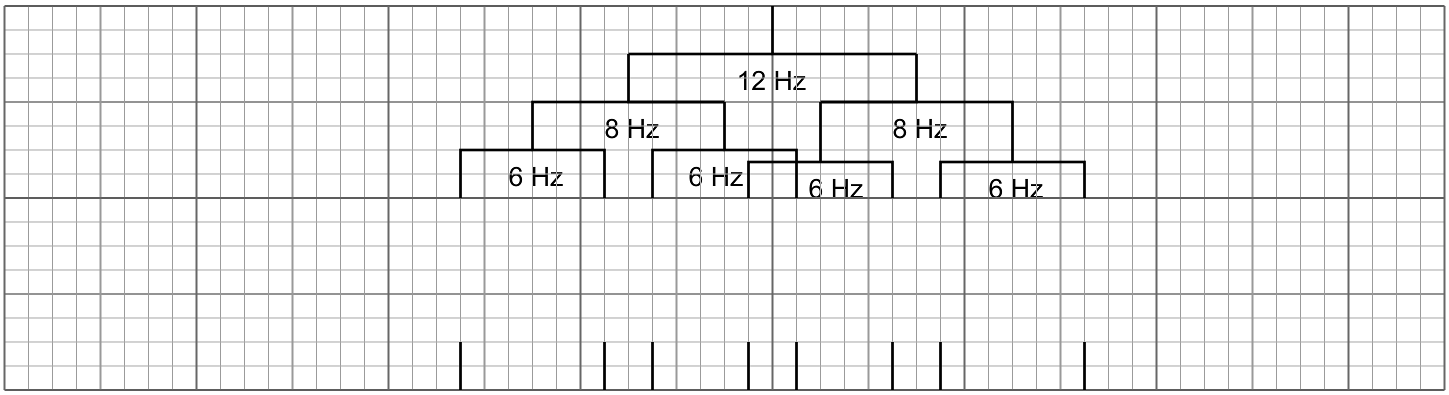


4.91 (dd, J = 17.5, 1.4 Hz, 1H)   4.83 (dd, J = 10.7, 1.4 Hz, 1H)

Doublet of Doublet of Doublets

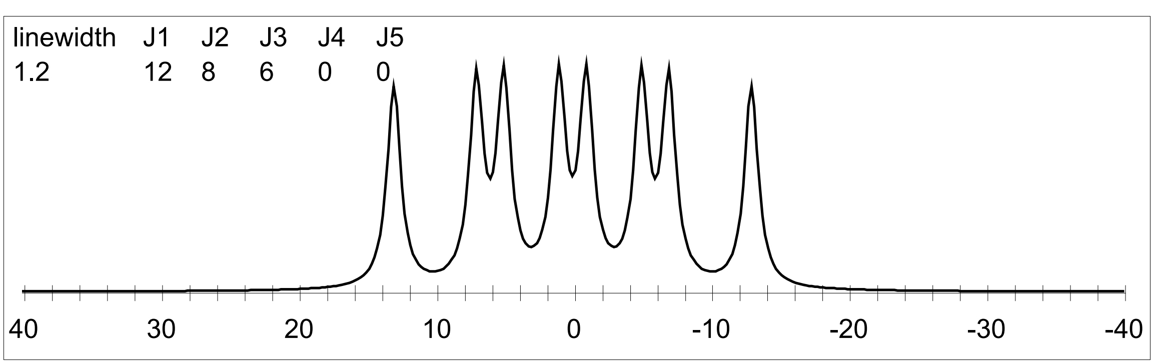
Description: A doublet of doublets of doublets (ddd) is a pattern of up to eight lines that results from coupling to three protons (or other spin 1/2 nuclei). The lines may be of all equal intensities (or close to equal intensities) or may overlap to give lines of greater intensities. If all of the coupling constants are the same, a quartet (q) occurs. If the two smaller coupling constants are the same, a doublet of triplets (dt) occurs. If the two larger coupling constants are the same a triplet of doublets (td) occurs.

Example: ddd, J = 12, 8, 6 Hz



The smallest J value of a ddd is always the distance between the first and second line (or the last and next to last line). The middle J value of a ddd is always the distance between the first and third line (or the last and second from last line). The largest J value of a ddd may be either the distance between the first and fifth line or the first and fourth, but is always the distance between the first and last lines minus the smallest and middle J values. (It is the distance between the first and fifth if the largest J is greater than the sum of the smaller two J's.)

Simulation of a ddd (J = 12, 8, 6 Hz) gives the the typical eight-line pattern.

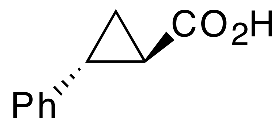


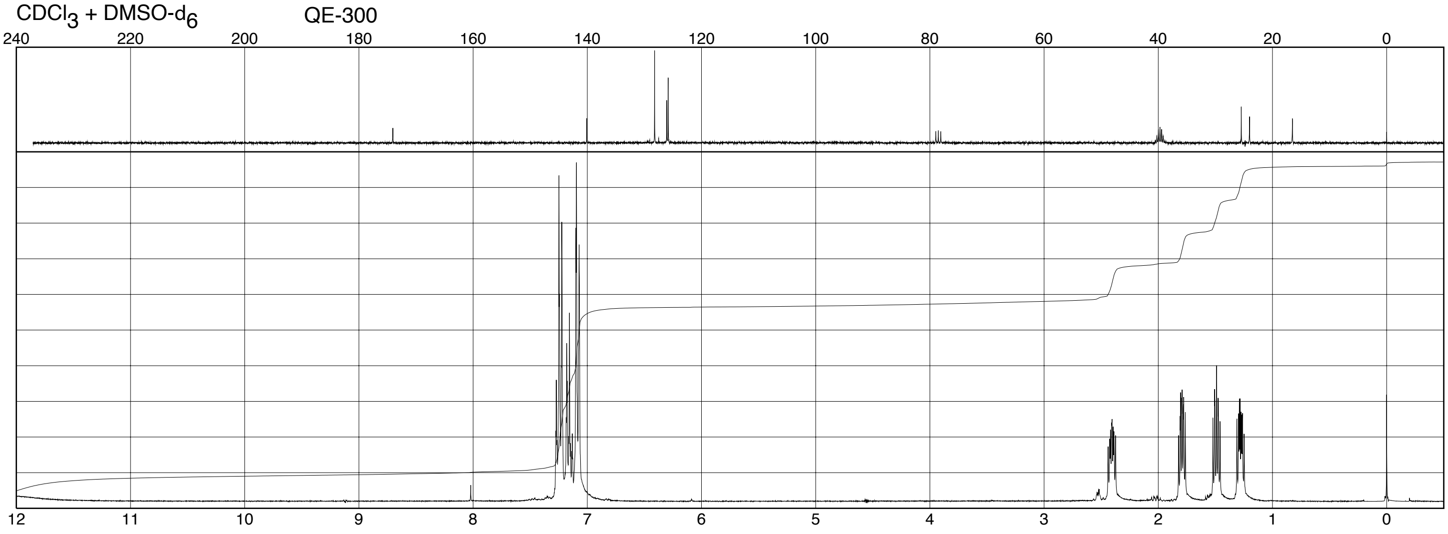
Doublet of Doublet of Doublets (continued)

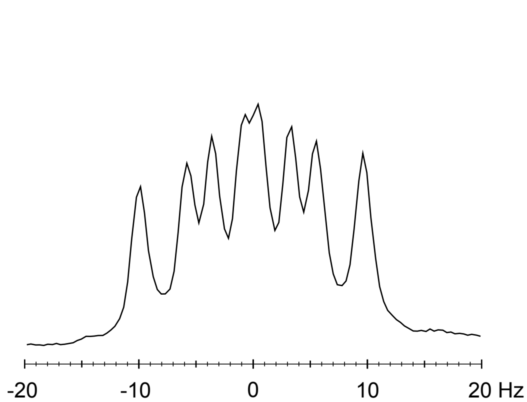
Example: ddd, J = 14, 10, 4 Hz (DRAW THE SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a ddd J = 14, 10, 4 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

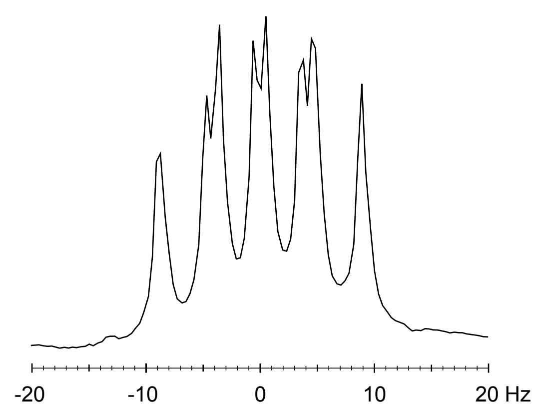
Doublet of Doublet of Doublets Examples: *trans*-2-Phenylcyclopropanecarboxylic acid



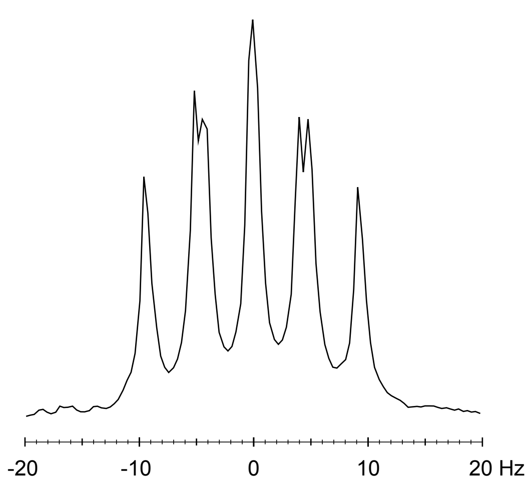




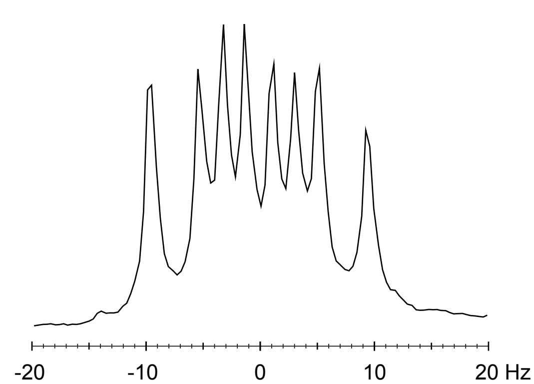
2.41 (ddd, J = 9.1, 6.3, 4.2 Hz, 1H)



1.79 (ddd, J = 8.3, 5.2, 4.2 Hz, 1H)



1.49 (ddd, J = 9.1, 5.2, 4.3 Hz, 1H)

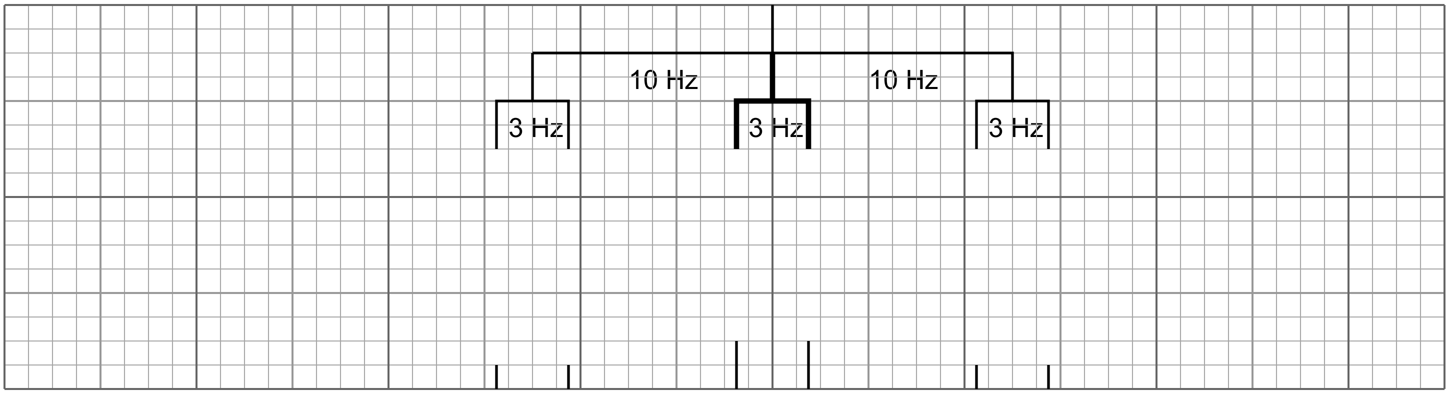


1.27 (ddd, J = 8.3, 6.3, 4.3 Hz, 1H)

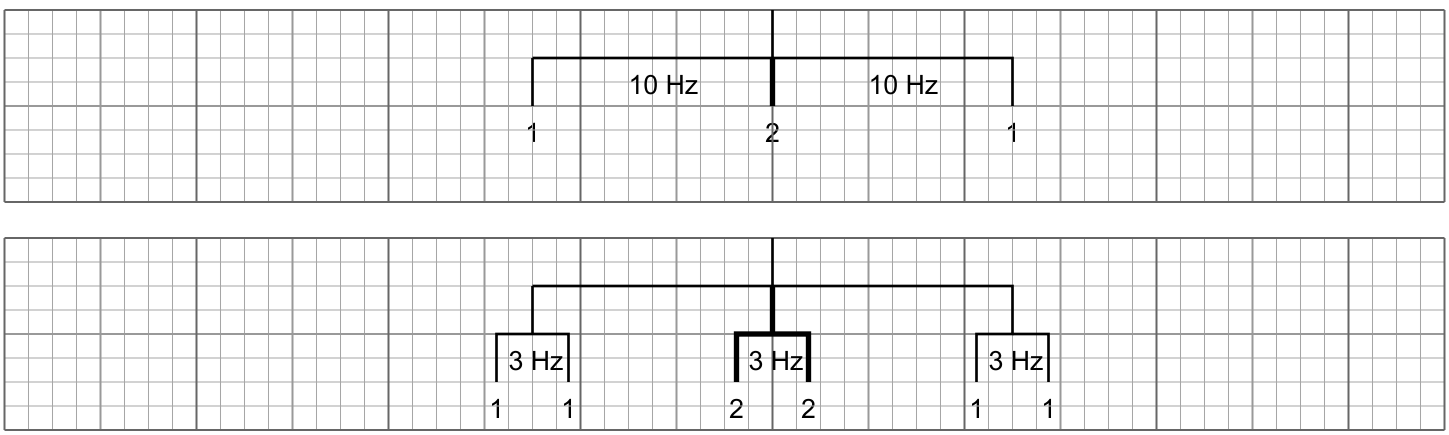
Triplet of Doublets

Description: A triplet of doublets (td) is a pattern of three doublets, in a 1:2:1 ratio of relative intensities, that results from coupling to two protons (or other spin 1/2 nuclei) with a larger *J* value and one proton (or other spin 1/2 nucleus) with a smaller *J* value.

Example: td, *J* = 10, 3 Hz

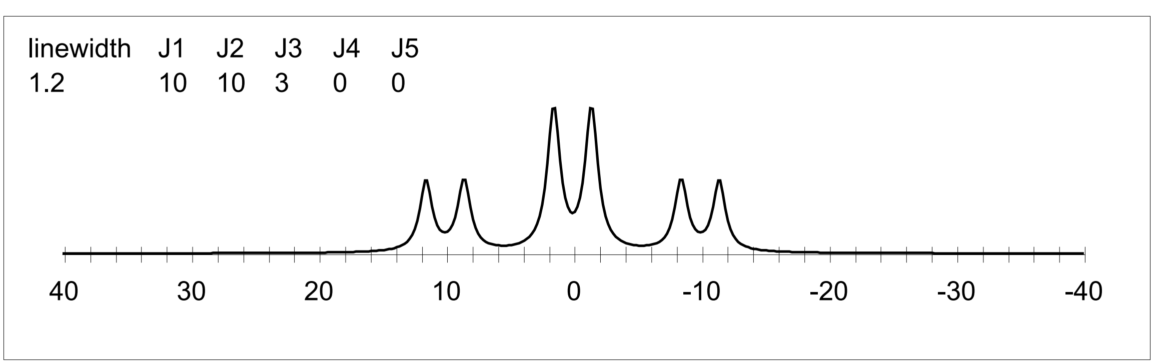


A triplet of doublets may be thought of as a triplet with 1:2:1 relative intensities. Each line of this triplet is further split into a doublet. The splitting tree has been represented as two successive drawings.



The *J* value of the doublet is always the distance between the first and second line (or the second and the third, or the fifth and the sixth). (I generally take the average of these values in analyzing the data.) The *J* value of the triplet is always the distance between the first and third line (the second and fourth, or the third and fifth, or the fourth and sixth. (I generally take the average of these values in analyzing the data.)

Simulation of a td *J* = 10, 3 Hz:

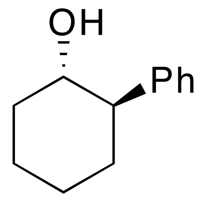


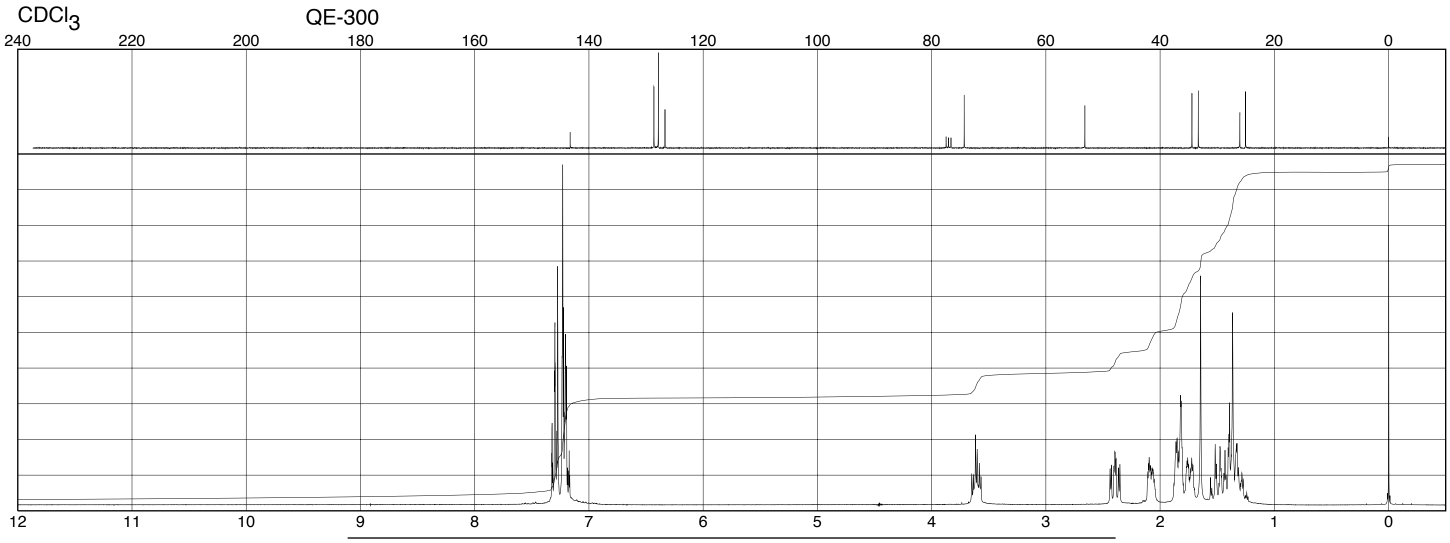
Triplet of Doublets (continued)

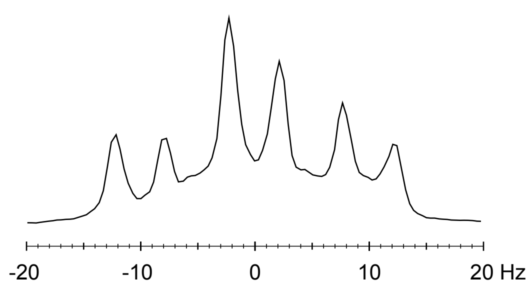
Example: td, J = 10, 7 Hz (DRAW A SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a td J = 10, 7 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

Triplet of Doublets Example: *trans*-2-Phenylcyclohexanol





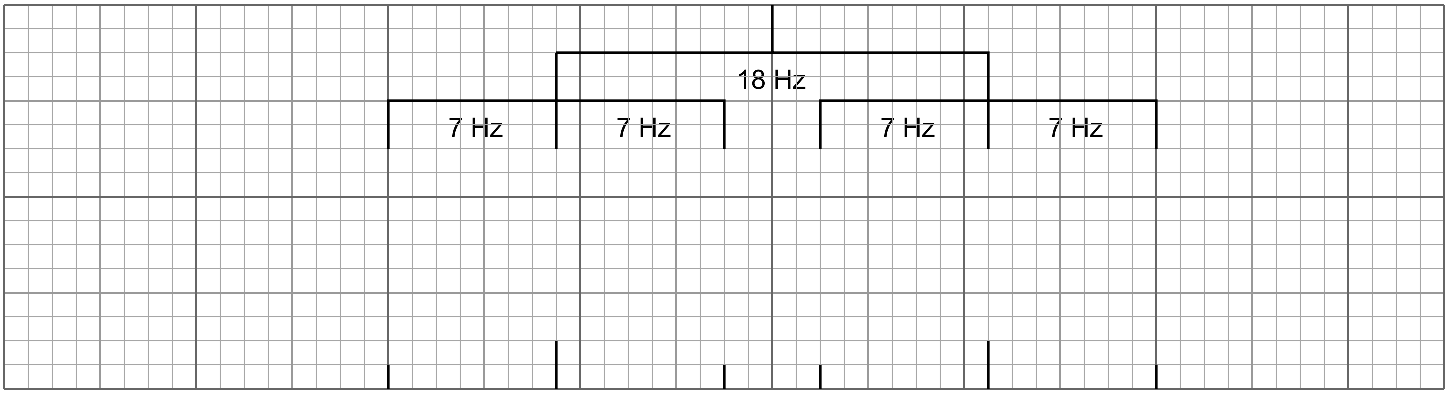


3.51 (td, J = 10.0, 4.4 Hz, 1H)

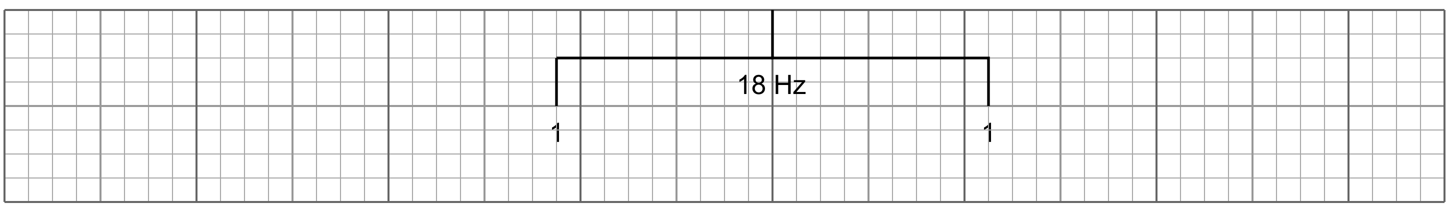
Doublet of Triplets

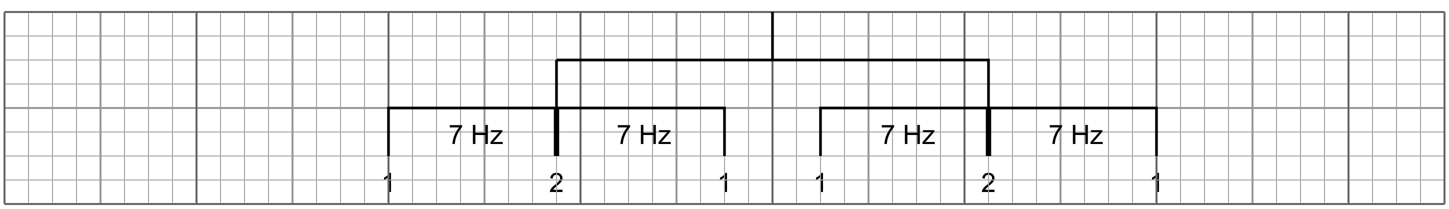
Description: A doublet of triplets (dt) is a pattern of two triplets, in a 1:1 ratio of relative intensities, that results from coupling to one proton (or other spin 1/2 nuclei) with a larger *J* value and two protons with a smaller *J* value.

Example: dt, *J* = 18, 7 Hz



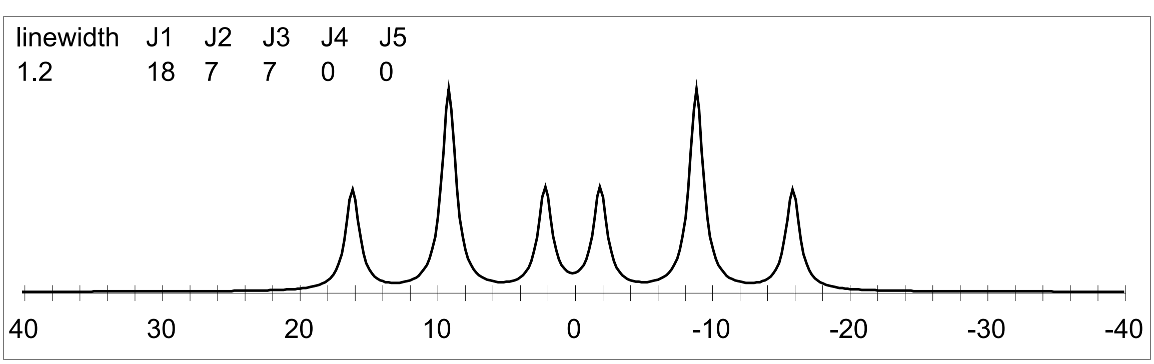
A doublet of triplets may be thought of as a triplet with 1:1 relative intensities. Each line of this doublet is further split into a tripletwith 1:2:1 relative intensities. The splitting tree has been represented as two successive drawings.





The smaller *J* value of a dt is always the distance between the first and second line (or the fifth and sixth). (I generally take the average of these values in analyzing the data.) The larger *J* value of a dt is always the distance between the second line and the fifth line (the two tall lines).

Simulation of a dt *J* = 18, 7 Hz:



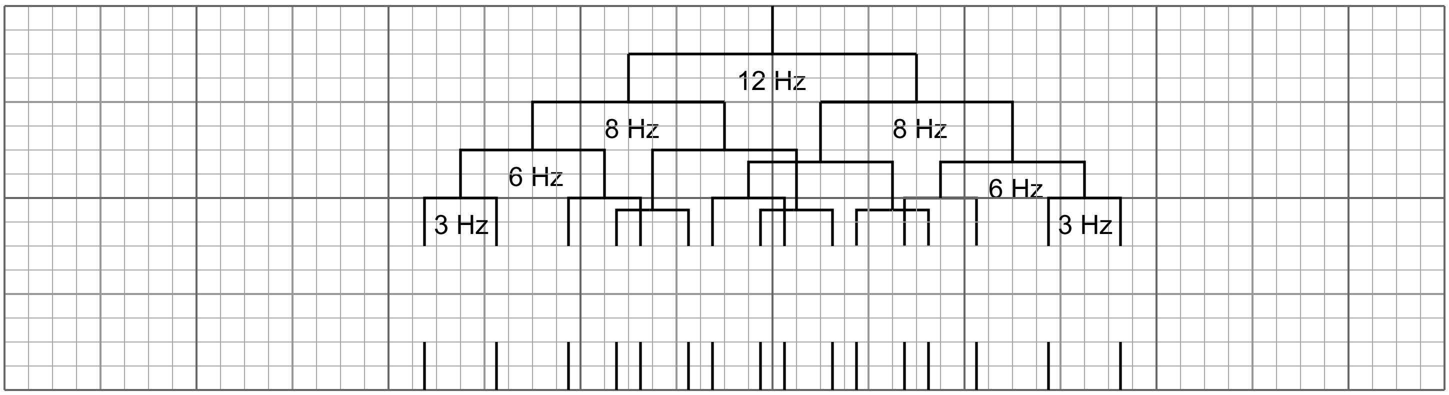
Doublet of Triplets (continued)

Example: dt, J = 10, 7 Hz (DRAW A SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a dt J = 10, 7 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

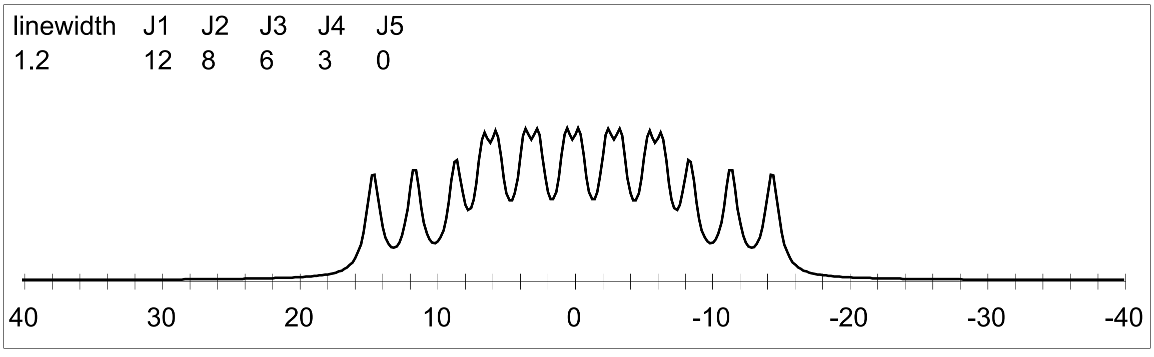
Doublet of Doublet of Doublet of Doublets

Description: A doublet of doublets of doublets of doublets (dddd) is a pattern of up to sixteen lines that results from coupling to four protons (or other spin 1/2 nuclei). The lines may be of all equal intensities (or close to equal intensities) or may overlap to give lines of greater intensities. If all of the coupling constants are the same, a quintet occurs. If the three smallest coupling constants are the same, a doublet of quartets (dq) results. If the three largest coupling constants are the same, a quartet of doublets (qd) results. If the two smallest coupling constants are the same, a doublet of doublet of triplets (ddt) occurs. If the two largest coupling constants are the same a triplet of doublet of doublets (tdd) occurs. If the two largest coupling constants are the same and the two smallest are the same a triplet of triplets (tt) occurs.



The smallest *J* value of a dddd is always the distance between the first and second line (or the last and next to last line). The next smallest *J* value of a dddd is always the distance between the first and third line (or the last and third from last line). The next-to-largest *J* value of a dddd may be either the distance between the first and fifth line or the first and fourth. (It is the distance between the first and fifth if the next-to-largest *J* is greater than the sum of the smallest two *J*'s.) The distance between the first and last lines is the sum of the four *J* values.

Simulation of a dddd (*J* = 12, 8, 6, 3 Hz)



Doublet of Doublet of Doublet of Doublets (continued)

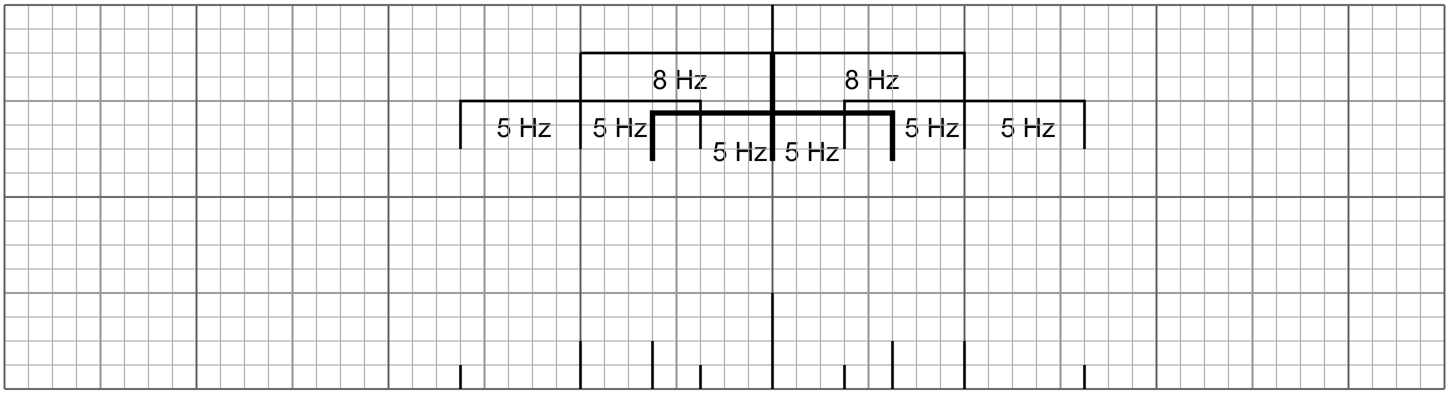
Example: dddd, J = 14, 10, 8, 4 Hz (DRAW THE SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a dddd J = 14, 10, 8, 4 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

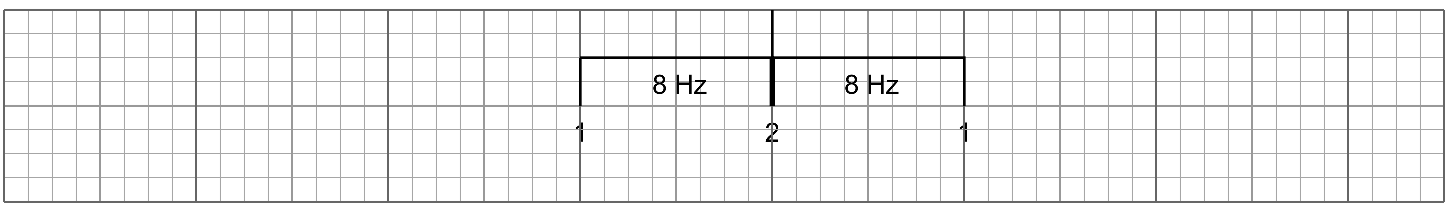
Triplet of Triplets

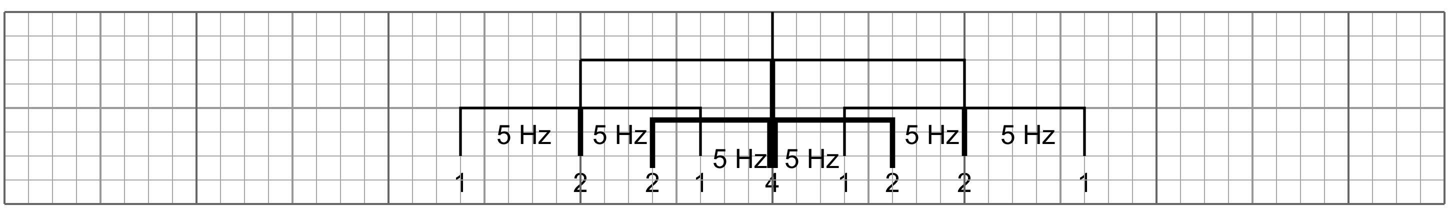
Description: A triplet of triplets (tt) is a pattern of three triplets, in a 1:2:1 ratio of relative intensities, that results from coupling to two protons (or other spin 1/2 nuclei) with one *J* value and two protons with another *J* value.

Example: tt, *J* = 8, 5 Hz



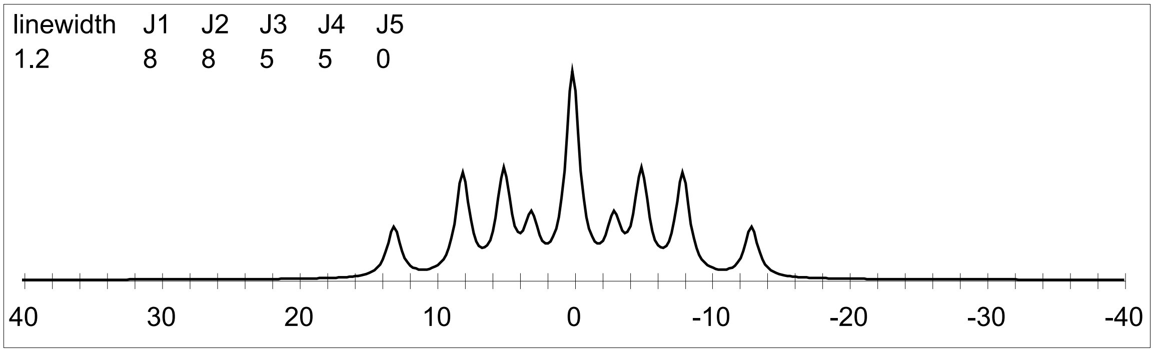
A triplet of triplets may be thought of as a triplet with 1:2:1 relative intensities. Each line of this triplet is further split into a triplet. The outer lines are split with 1:2:1 relative intensities, and the more intense inner line is split with 2:4:2 relative intensities. The splitting tree has been represented as two successive drawings.





The smaller *J* value of a tt is always the distance between the first and second line (or the last and next to last line). The larger *J* value of a tt is always the distance between the second line and the middle (tallest) line (or the middle line and the and the next to last line) and may also be measured as half the distance between the second line and the next to the last line.

Simulation of a tt *J* = 8, 5 Hz:

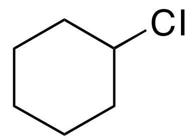


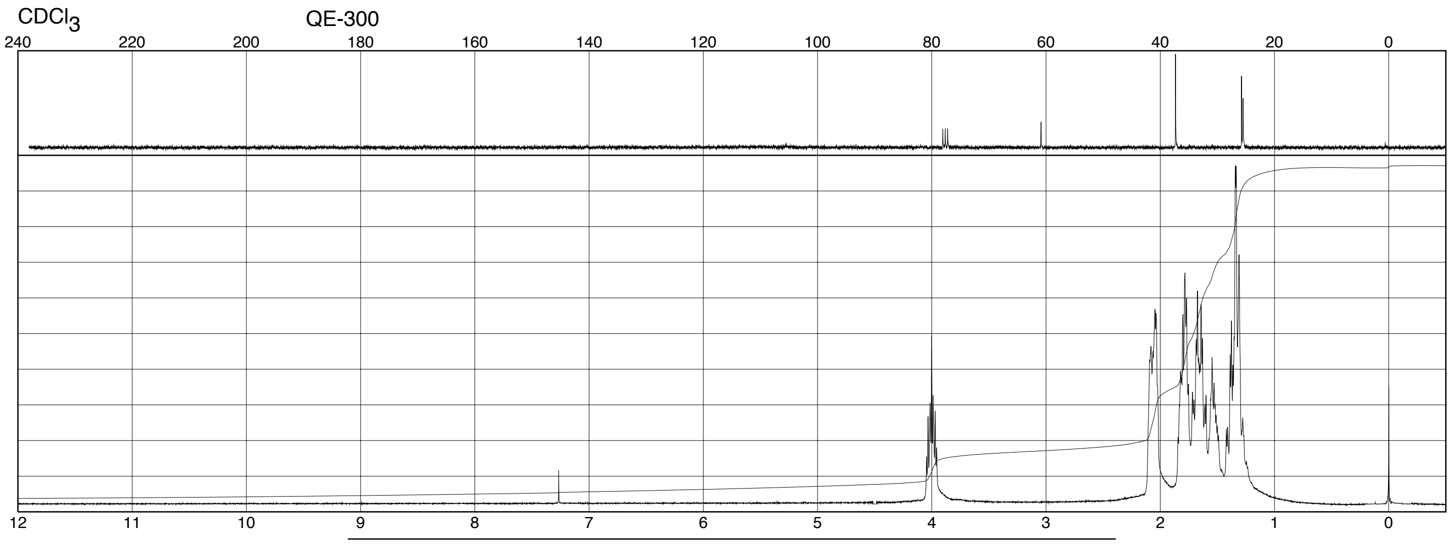
Triplet of Triplets (continued)

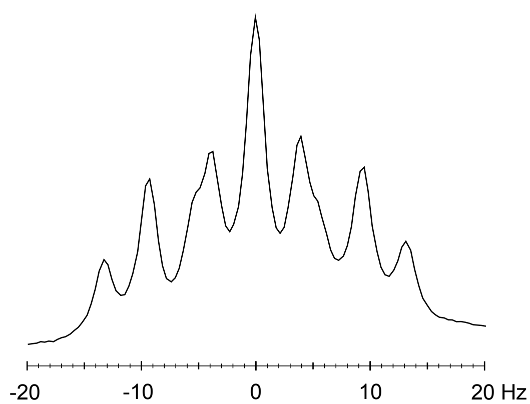
Example: tt, *J* = 7, 2 Hz (DRAW A SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a tt *J* = 7, 2 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

Triplet of Triplets Example: Chlorocyclohexane





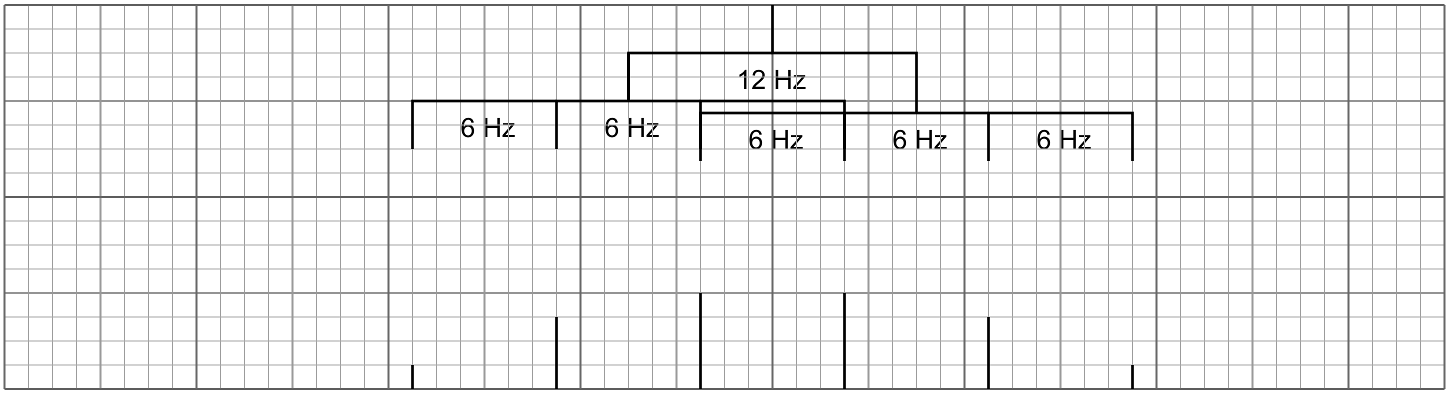


4.00 (tt *J* = 9.3, 3.9 Hz, 1H)

Doublet of Quartets

Description: A doublet of quartets (dq) is a pattern of two quartets that results from coupling to one proton (or other spin 1/2 nuclei) with a larger *J* value and three protons (or other spin 1/2 nuclei) with a smaller *J* value.

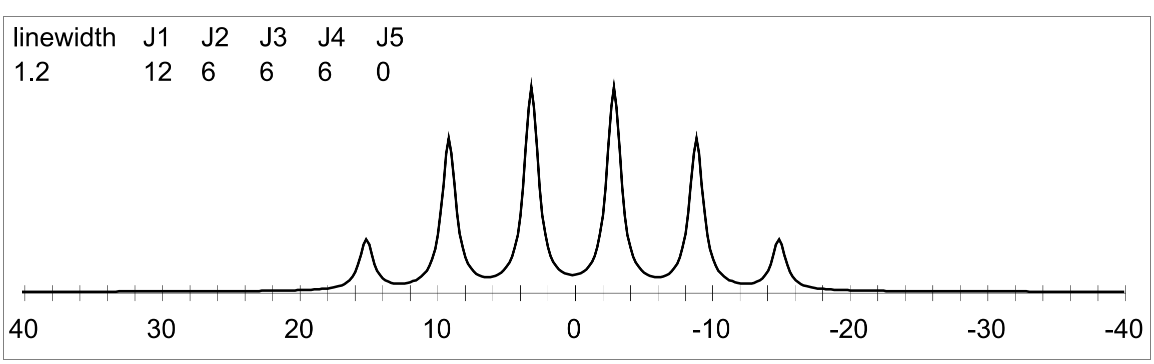
Example: dq, *J* = 12, 6 Hz



This is an interesting example of a dq, because the characteristic 1:3:3:1 relative intensity patterns of the quartets are obscured by overlap and together result in a 1:3:4:4:3:1 pattern, which would be easy to mistake this pattern for the 1:5:10:10:5:1 pattern of a sextet. The worksheet on the next page provides a pattern that is easier to recognize as a pair of overlapping 1:3:3:1 patterns.

The smaller *J* value of a dq (the *J* value of the quartets) is always the distance between the first and second line (or the last and next to last line). The larger *J* value of a dq (the *J* value of the doublets) is always the distance between the first and third of the tall lines (or the second and fourth of the tall lines). The larger *J* is also the distance between the second line and the next to last line minus the smaller *J* value.

Simulation of a dq *J* = 12, 6 Hz:

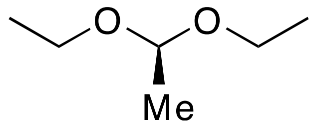


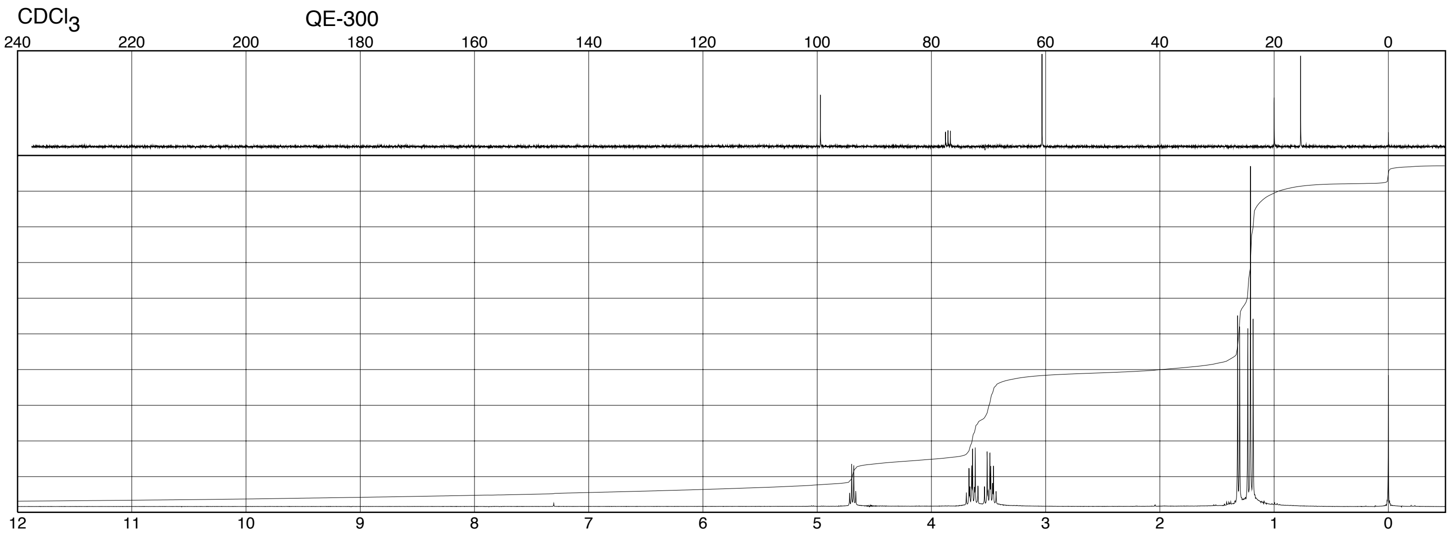
Doublet of Quartets (continued)

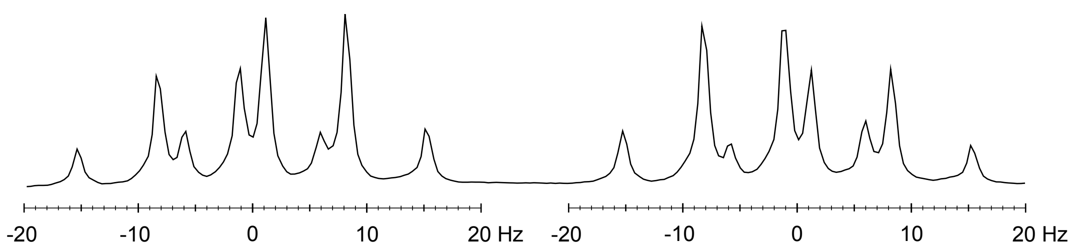
Example: dq, J = 14, 6 Hz (DRAW A SPLITTING TREE AND GRAPH THE MULTIPLET. Use a scale of 1 box is equal to 1 Hz on the horizontal axis and accurately represent the relative heights of the lines on the vertical axis.)

Simulation of a dq J = 14, 6 Hz (PROVIDE A SIMULATION USING THE "MultipleHz.xls" SPREADSHEET)

Doublet of Quartets Examples: Acetal







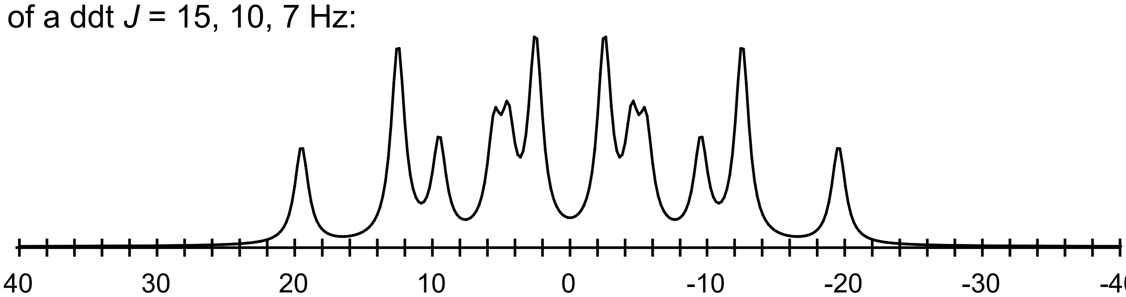
3.64 (dq, J = 9.4, 7.1 Hz, 2H)   3.47 (dq, J = 9.4, 7.1 Hz, 2H)

Doublet of Doublet of Triplets (ddt), Doublet of Triplet of Doublets (dtd), and Triplet of Doublet of Doublets (tdd)

Description: The ddt, dtd, and tdd patterns consist of up to 12 lines and contain lines in 1:2 ratios of intensities. These patterns all result from coupling to four protons (or other spin 1/2 nuclei), two of which with the same *J* values and two of which with different *J* values. In a ddt, the two smallest couplings have the same *J* value; in a dtd, the two mid-sized couplings have the same *J* value; in a tdd, the two largest couplings have the same *J* value.

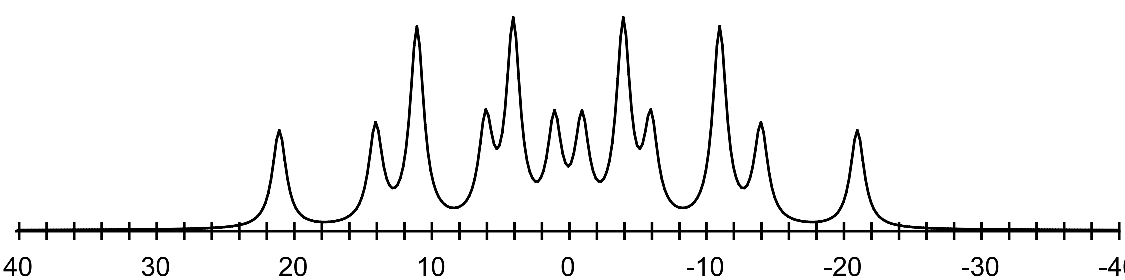
In a doublet of doublet of triplets (ddt), the second line is twice the height of the first line. The smallest *J* is the *J* associated with the triplet and is the distance between the first and second line (or the last and next to last line). The mid-sized *J* is either the distance between the first and third line or the first and fourth line if the third line is part of the triplet. The largest *J* is always the distance between the first and last lines minus the middle and twice the smallest *J* values.

Simulation of a ddt *J* = 15, 10, 7 Hz:



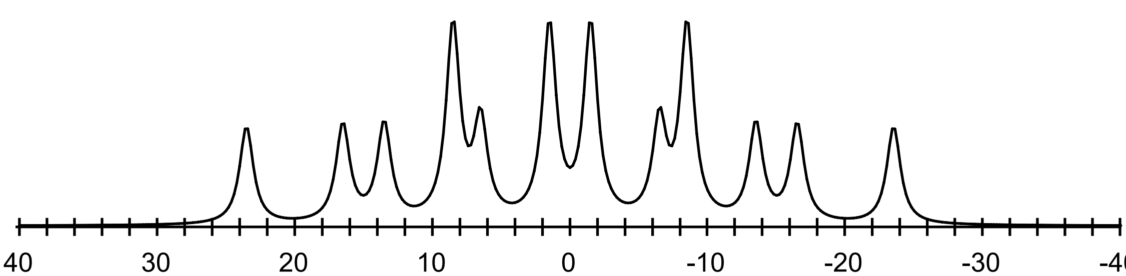
In a doublet of triplets of doublets (dtd), the third line is twice the height of the first line. The smallest *J* is the distance between the first and second line (or the last and next to last line). The mid-sized *J* associated with the triplet and is the distance between the first and third line (or the last and second from last line). The largest *J* is always the distance between the first and last lines minus the smallest and twice the middle *J* values.

Simulation of a dtd *J* = 15, 10, 7 Hz:

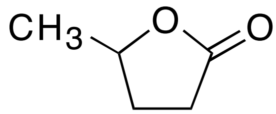


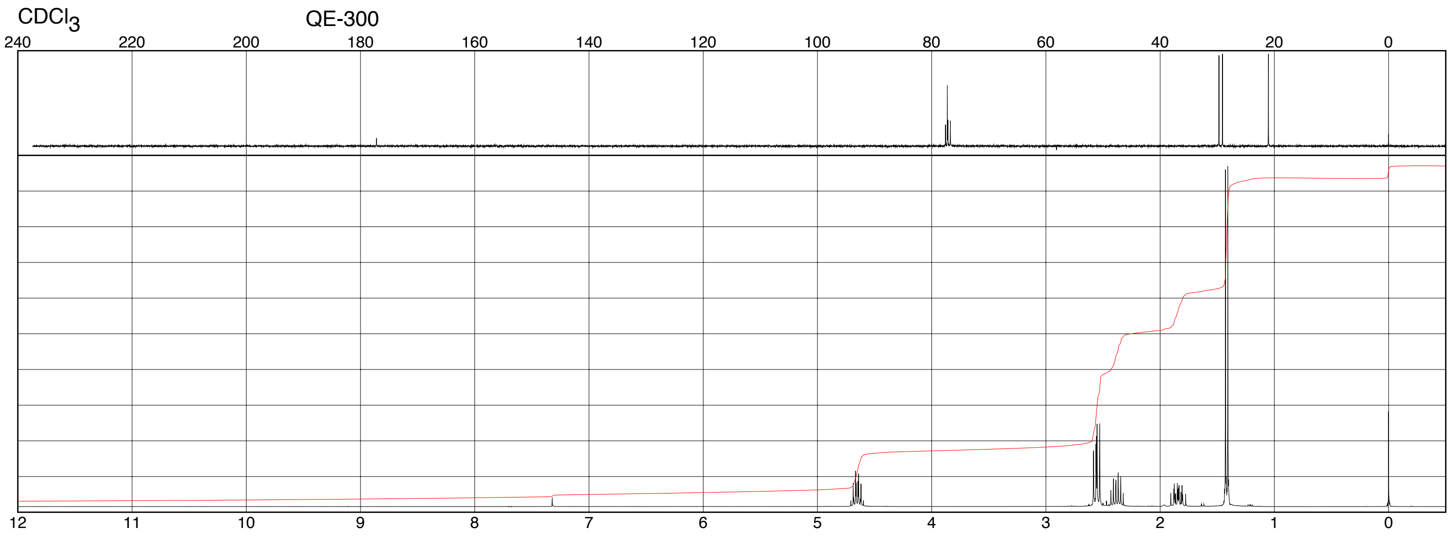
In a triplet of doublets of doublets (tdd), the fourth or fifth line is twice the height of the first line. The smallest *J* is the distance between the first and second line (or the last and next to last line). The mid-sized *J* is the distance between the first and third line (or the last and second from last line). The largest *J* is always one half of the quantity given by the distance between the first and last lines minus the smallest and mid-sized *J* values.

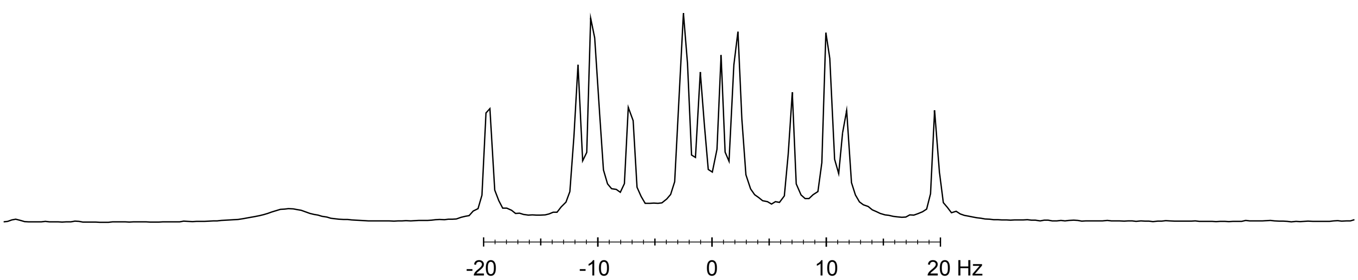
Simulation of a tdd *J* = 15, 10, 7 Hz:



Doublet of Triplet of Doublet of Doublets Example: γ-Valerolactone







1.84 (dtd, J = 12.6, 9.4, 7.9 Hz, 1H)