Multi-frequency Homonuclear Decoupling with VnmrJ 3.1 Software

Application Note

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Homonuclear decoupling experiments enable users to both detect scalar couplings between different nuclei and measure the magnitude of coupling constants. They are a viable alternative to 2D COSY experiments for the determination of coupling constants and they potentially offer more accuracy. Virtually all applications of NMR can make use of the information gained from homonuclear decoupling experiments, especially when working with compounds whose molecular weights are less than a few thousand. A 1D homonuclear decoupling experiment is usually the best choice if the structure of the sample is known, whereas a 2D homonuclear experiment is typically better for compounds whose structure is not known. Traditional homonuclear decoupling methods, however, can be time-consuming and tedious when dealing with compounds whose spectra contain many multiplets. This technical overview describes a unique multi-frequency homonuclear decoupling capability in the VnmrJ 3.1 software that can simultaneously irradiate many multiplets, which can eliminate several steps and speed the decoupling process.

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Irradiating more than one multiplet, simultaneously

VnmrJ3.1 software makes it just as easy to irradiate numerous multiplets as it is to irradiate one, which is very useful for analyzing complex spectra. To acquire a homonuclear decoupling experiment using the foreground mode of acquisition, the ^{1}H spectrum of the sample of interest is displayed in the graphics window, and the "(H) HomoDec" protocol button is selected (Figure 1). This loads the HomoDec experiment into the foreground parameter set and leaves the spectrum in the graphics window, to allow the user to graphically select the multiplets to be irradiated. The selection process is done in conjunction with the HomoDec Acquire/Default parameter page as is shown in Figure 2.

The "Multifrequency decoupling" box in Figure 2 must be checked (selected) before choosing any spectral regions for decoupling , in order to simultaneously irradiate several spectral regions in one experiment. Using the graphics window, the left and right cursors are then placed around a multiplet to be irradiated, and the "Select" button is pressed (bottom center of Figure 2). Each time a multiplet is bracketed, the "Select" button is pressed again so as to add that multiplet to the list of regions to be irradiated. (To reset the list of regions, the "CLEAR" button is pushed, and the regions of interest are selected again.) Once all multiplets of interest are selected, the green 'Acquire' button is clicked to start the acquisition.

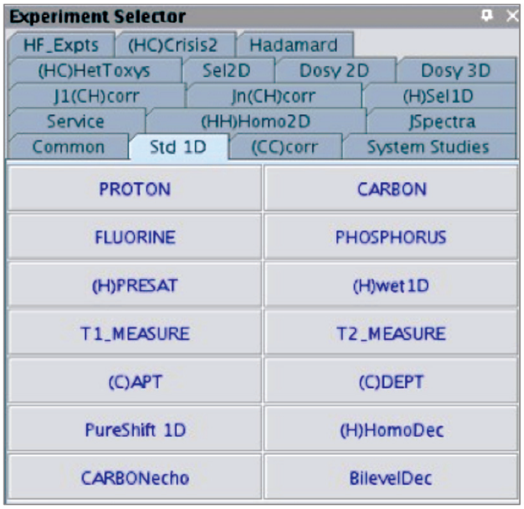
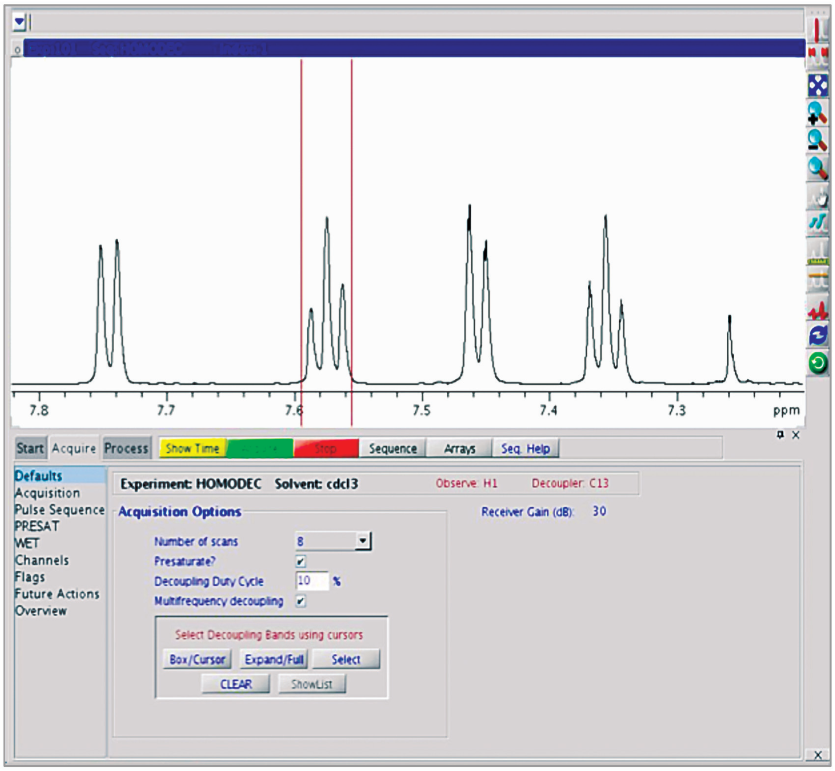


Figure 1. The "Experiment Selector" vertical panel, showing the "(H)HomoDec" protocol button.



Experiment: HOMODEC Solvent: cdcl3 Observe: H1 Decoupler: C13

Receiver Gain (dB): 30

Number of scans 8

Presaturate? ☑

Decoupling Duty Cycle 10 %

Multifrequency decoupling ☑

Figure 2. The Acquire/Default parameter page for the HomoDec experiment as it appears when using the foreground mode of acquisition, and showing the "Multifrequency decoupling" box selected (checked). The graphics area above it shows the expanded proton spectrum as well as the cursors positioned around the first region to be selected for irradiation.

Deconvoluting a complex structure with multi-frequency irradiation

The VnmrJ 3.1 software includes the unique Pbox algorithm that automatically constructs a single multi-frequency shape file on the fly, which allows the user to irradiate all of the selected multiplets simultaneously in one single experiment. This has two major benefits over existing methods. First, it takes less time to acquire one spectrum in which several multiplets were irradiated simultaneously than it takes to acquire an array of spectra in which each multiplet is sequentially irradiated. Secondly, the spectrum will be simplified from decoupling all of the multiplets at once. The two benefits can lead to a direct interpretation of the result, and do so in less time than it takes to infer the result from spectra collected as an array.

The top spectrum in Figure 3 illustrates the utility of simultaneous irradiation of multiplets, using 2-ethyl-indanone in $CDCl_3$ as the sample. A simple analysis of this data can be done as follows. A comparison of the bottom (control) spectrum to the middle spectrum shows that the triplet at 7.58 ppm is coupled to both the doublet at 7.46 ppm and the triplet at 7.36 ppm. The triplet at 7.36 ppm is coupled to yet another resonance, because it remains a doublet when 7.58 ppm is irradiated. The doublet at 7.75 ppm is not coupled to the signal at 7.58 ppm (because it remains a doublet in the middle spectrum). By irradiating both the 7.36 ppm signal and the 7.58 ppm signal as shown in the top spectrum, it can then be seen that the 7.75 ppm doublet is coupled to the 7.36 ppm triplet, which is coupled to the 7.58 ppm triplet, which is then coupled to the 7.46 ppm doublet. This traces out the bonding order of the four protons by simple inspection. These protons undoubtedly are located on the ortho-substituted phenyl ring shown in the structure of 2-ethyl-indanone (Figure 3). By itself, this data doesn't show which proton of the chain lies closest to the carbonyl carbon, but other experiments such as heteronuclear multiple bond correlation (HMBC) NMR can determine this.

Conclusions

Homonuclear decoupling experiments can provide a wealth of structural information, but they can be tedious to perform using traditional methods. Irradiating each multiplet one-at-a-time, or even as an array of single-irradiation experiments, can be both tedious and time-consuming to set up, and data acquisition can also be very slow. Using the new multi-frequency irradiation feature in VnmrJ 3.1 software, several multiplets can be chosen and irradiated simultaneously, with as little effort as it previously took to irradiate one. Very complex structures can now be elucidated much faster, while requiring much less interaction from the investigator.

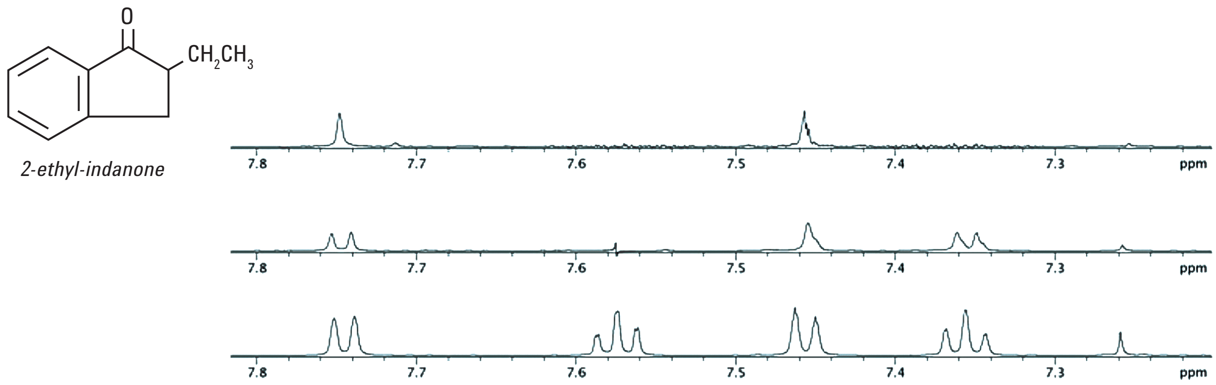


Figure 3. An example of Homonuclear Decoupling data on 2-ethyl-indanone (structure shown above spectra) acquired by irradiating more than one multiplet at once, simultaneously, in one experiment. The bottom spectrum is a simple 1D ^{1}H spectrum, expanded to show only the four protons in the aromatic region. The top two spectra were both acquired with the HomoDec experiment by irradiating either the triplet at 7.58 ppm (one multiplet; middle spectrum) or both triplets at 7.58 and 7.36 ppm (two multiplets; top spectrum).

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