

Decoupling Theory and Practice

General Concepts

We have spent the last two lectures discussing the structural implications of J -coupling analysis and overall have discovered that the interaction may readily be exploited to generate both qualitative as well as quantitative structural information.

Now we're going to throw it all away!

The technology of spin-decoupling, or commonly simply, *decoupling*, maintains fundamental importance in modern NMR spectroscopy.

The goal of decoupling is to reduce the magnitude of the J -coupling interaction to an arbitrary small value.

Perhaps the fundamental question should be: Why throw away perfectly good structural information?

As we have seen, for a small number of well-separated resonances, resonance fine-structure due to J -coupling adds information to the spectrum – however we have also had hints that too much of a good thing is just that can obscure information.

J -coupling can lead to splitting that in turn may complicate the analysis of chemical shifts. In some cases one splitting can even complicate the interpretation of other J -couplings.

Sometimes less is more, i.e., a less complicated spectrum can provide more definitive information.

Another important issue is sensitivity.

The presence of J -coupling generally leads to a splitting of the resonance into several less intense resonance 'peaks', i.e., spectral features characterized by amplitude and shape.

Given any noise level (amplitude or power), coupled peaks will have lower signal-to-noise (S/N) ratios than will their uncoupled (decoupled) equivalents.

The decrease in sensitivity due to coupling clearly depends upon the specific coupling pattern involved – a resonance split into a doublet will have about half the S/N of the equivalent uncoupled or decoupled resonance.

Removing the coupling effects from spectrum can thus lead to $> 2\times$ increase in the S/N.

Recall that a signal is coherent and may be accumulated using coaddition of signals from multiple experiments. The signal amplitude increases as N , the number of experiments or transients.

True noise by definition is random or uncorrelated. Perhaps surprisingly in a coaddition scheme the amplitude of the noise also increases (though not as rapidly as coherent signal) and depends upon \sqrt{N} .

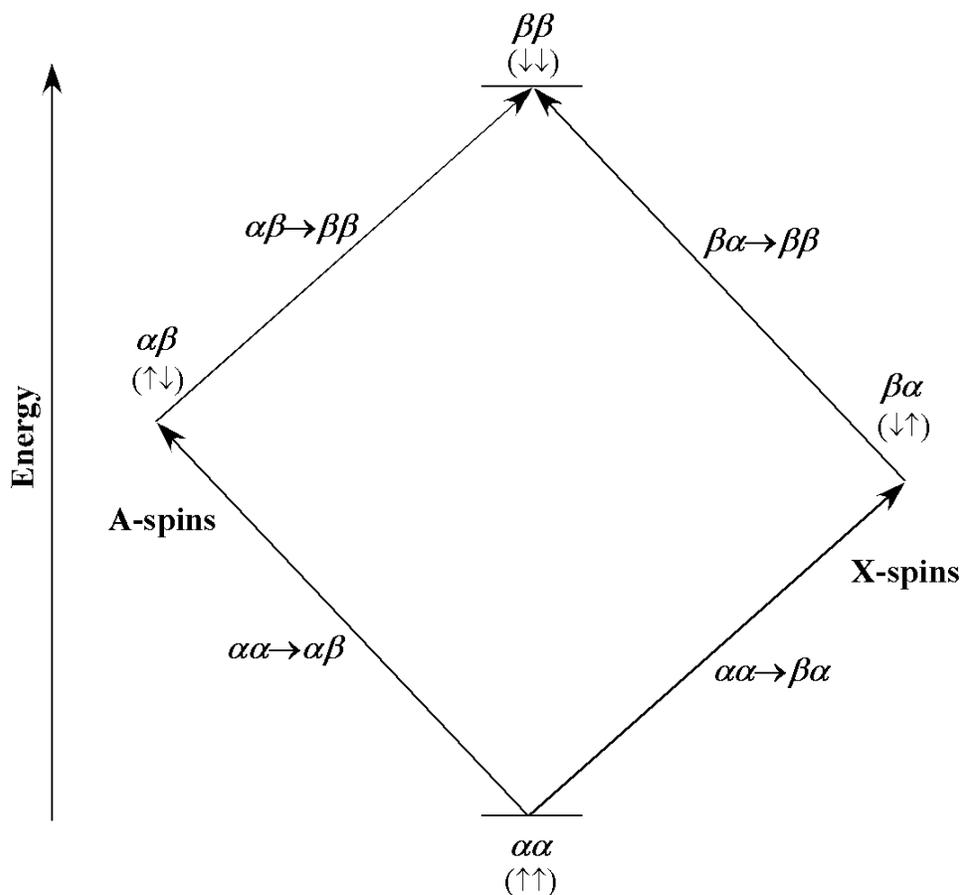
Overall, one would have to sum $4\times$ experiments to increase the S/N by a factor of $2\times$ – by comparison, the improvement in sensitivity obtainable through decoupling can be substantial.

Although isotopic enrichment (deuteration) can be used to reduce or eliminate J -coupling effects, it will generally be more straightforward to *effectively* eliminate the effects of the coupled spin.

The solution to this sort of problem has been addressed in a general theoretical way by physics. The solution involves interfering with an interaction in such a way as to average its influence to an arbitrarily small value, and is dealt with in detail by *average Hamiltonian theory*.

The interaction energy of the indirect spin-spin coupling depends upon the relative quantum states of the two coupled spins – if the nuclear spins are paired, then the electron spins can also pair and the net energy of the system is lowered, and *vice versa*.

Energy Level Diagram of the Coupled AX Spin System



The energy of the J -coupled spin spins states is given by the following expressions:

$$\begin{aligned}
 E(\alpha\alpha) &= -\frac{1}{2}(v_A + v_X) + \frac{J_{AX}}{4} & E(\alpha\beta) &= \frac{1}{2}(-v_A + v_X) - \frac{J_{AX}}{4} \\
 E(\beta\alpha) &= \frac{1}{2}(v_A - v_X) - \frac{J_{AX}}{4} & E(\beta\beta) &= \frac{1}{2}(v_A + v_X) + \frac{J_{AX}}{4}
 \end{aligned}$$

Note that it is actually the transition energies that are measured:

A-spin Transition Energies:

$$(\alpha\alpha \rightarrow \beta\alpha) = \nu_A - \frac{1}{2}J_{AB}$$

$$(\alpha\beta \rightarrow \beta\beta) = \nu_A + \frac{1}{2}J_{AB}$$

X-spin Transition Energies:

$$(\alpha\alpha \rightarrow \alpha\beta) = \nu_X - \frac{1}{2}J_{AB}$$

$$(\beta\alpha \rightarrow \beta\beta) = \nu_X + \frac{1}{2}J_{AB}$$

This is exactly what we see experimentally for an AX-spin system, 1:1 doublets split symmetrically by $J_{AX}/2$ on either side of the uncoupled resonance frequency.

In an A–X spin system, if monochromatic RF irradiation (energy) is supplied at the X-spin frequency, the populations of the energy levels of the X-spin will become equal, and will remain equalized so long as the RF irradiation persists. This effect is known as *saturation*.

Saturation appears to be a static condition, i.e., the irradiated spin is held in a saturated state so long as the RF irradiation persists.

As has been true for many of the glib and simple explanations we have encountered thus far, this picture is too simple.

We have discussed the issues associated with the magnitude of the energies of NMR excited states, and emphasized that transition to excited states as well as relaxation from these states must be *stimulated* by fluctuating fields with Fourier component extant at the resonant frequency.

Later in the course we will discuss intrinsic sources of such stimulating fields (intramolecular reorientational motion). Here it is sufficient to recognize that the exciting RF radiation is in fact capable of stimulating both absorption *and* emission of energy.

Thus, while it is initially true that net energy is absorbed by the spin system, as additional RF energy is applied, the spins are *stimulated* to emit *and* absorb energy, maintaining the saturation condition.

The mechanics of this dynamical state may be rigorously examined. If one of the spins, X, is subjected to RF irradiation of the appropriate intensity and frequency, the spin state will continuously vary between $+1/2$ and $-1/2$.

If the interconversion rate is high enough, the A spins will see only the *average* of the X spin state, which is zero. Spectra recorded will no longer contain the X-spin resonance, and the A spin will no longer exhibit splitting.

This then is the decoupling condition, the irradiated spin is continuously absorbing and emitting energy in a *dynamical* condition.

The method outlined here, the application of monochromatic RF irradiation at the resonance frequency of a particular spin (X), is known as *selective decoupling*.

Selective decoupling is one type of a large class of experiments known as *double-resonance* methods. The nomenclature here is that the main excitation RF field is labeled B_1 and a second field will be labeled B_2 and any experiment that employs RF irradiation is known as a *double-resonance* technique.

This nomenclature is a historical artifact which can generate some confusion if older and newer methods are discussed in the same context.

In modern parlance, double resonance refers to multinuclear techniques and often implies multidimensionality as well.

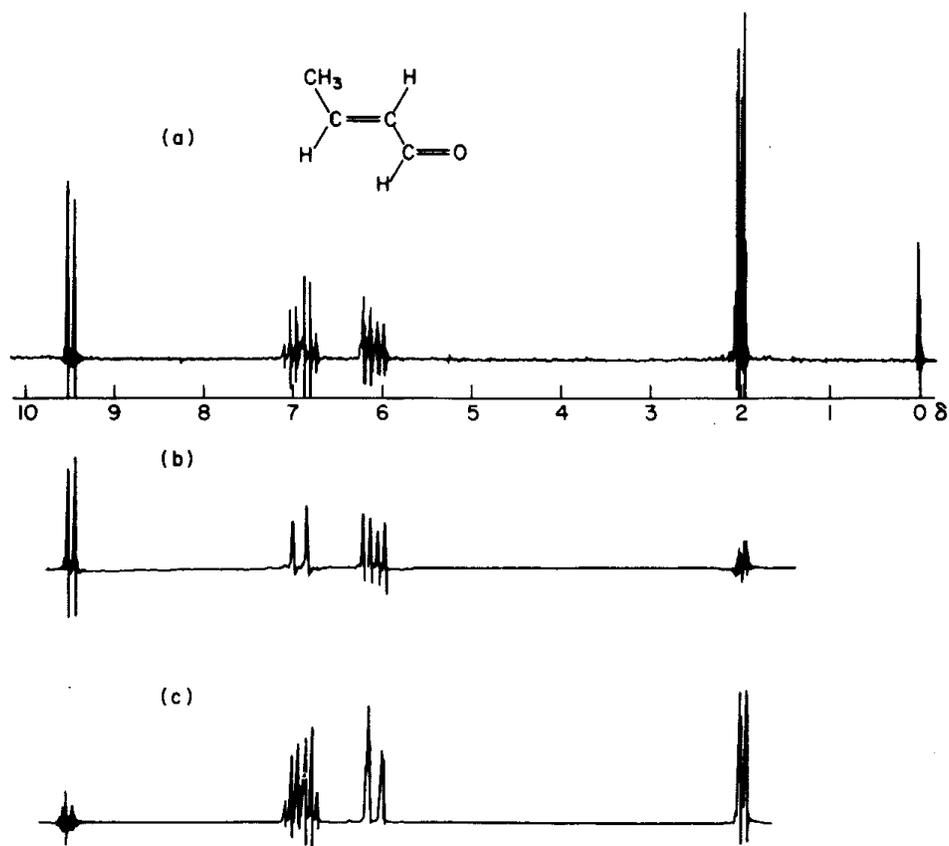


Figure 6.1 from Abraham, R.J., Fisher, J. and Loftus, P. (1988) Introduction to NMR Spectroscopy. John Wiley and Sons, New York

- Figure: a) CW spectrum of ^1H spectrum of crotonaldehyde
 b) Spectrum with monochromatic irradiation of the methyl resonance
 c) Spectrum with monochromatic irradiation of the aldehyde resonance

The spectrum shown was recorded using a CW NMR instrument, which is why the resonances in the crotonaldehyde figure the characteristic ringing pattern in their fine structure.

The irradiated resonance is never completely eliminated from the spectrum as is clearly visible in both the middle and lower figures of the crotonaldehyde spectrum.

In the scheme outlined above, each chemical shift (central frequency) could be probed with RF irradiation, and the resulting decoupling influences inspected and tabulated based on the resulting data.

A central practical consideration is what RF power is sufficient to decouple a particular resonance.

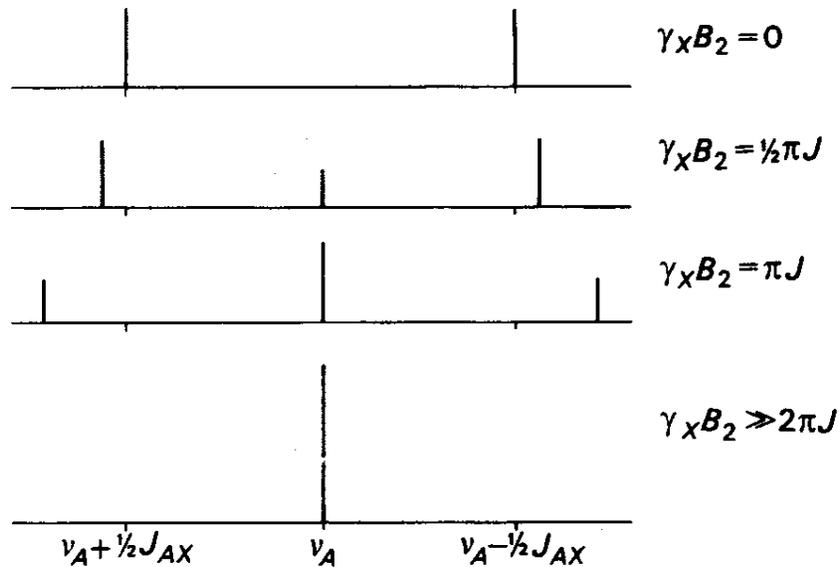


Figure 4.7 from Harris, R.K. (1986) Nuclear Magnetic Resonance Spectroscopy. John Wiley and Sons, New York.

Assume that the J-coupling values is 10 Hz, and to be certain that we are supplying sufficient RF power, we will set the value of $\gamma_X B_2$ to be $10 \times 2\pi J$. The strength of the RF field required we therefore be:

$$\gamma_x = \gamma_H = 267.522 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$$

$$B_2 = 10 \frac{2\pi J}{\gamma_x} = 10 \frac{2(3.1415)(10 \text{ s}^{-1})}{(267.522 \times 10^6 \text{ s}^{-1} \text{ T}^{-1})} = 2.35 \times 10^{-6} \text{ T} = 2.35 \times 10^{-2} \text{ G}$$

This very small field can be effective, because it is resonant, i.e, precisely at the resonance frequency of the X-spin.

In practice, the spectroscopist rarely has an accurate calibration between the output power of the RF amplifier and the effective field produces in the transmitter coil, and proper decoupling conditions are established semi-empirically.

The advantages of such a selective decoupling experiment is clear – only the desired spin is saturated, allowing for a relatively simple *sequential/deductive* succession of experiments to be considered as demonstrated for the crotonaldehyde example.

The approach is concise, complete and the interpretation of results often provides a key one-to-one correspondence between ^1H and ^1H resonances or between ^1H and ^{13}C resonances that may be interpreted *by inspection*.

The figure below demonstrates the effect of selective irradiation of the ε proton resonance in histidine on the ^{13}C spectrum of that molecule.

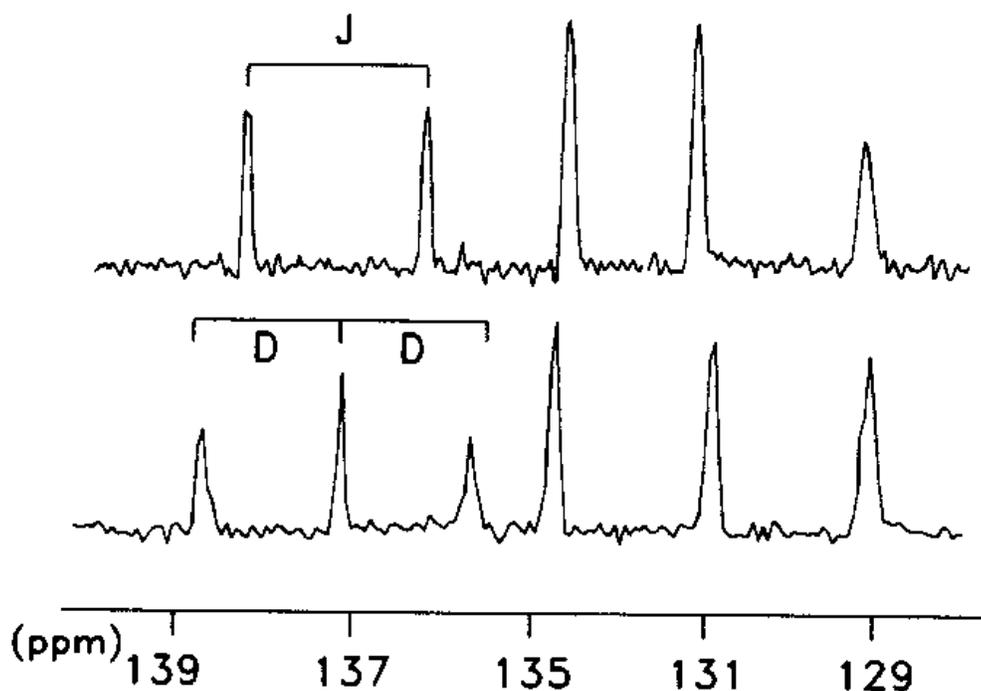


Figure 3.35 from van de Ven, F.J.M. (1995) *Multidimensional NMR in Liquids*. Wiley-VCH, New York.

One limitation of the method is its intrinsically low efficiency – since a narrow frequency bandwidth is employed (monochromatic or semi-selective) only a subset of the spin network will be decoupled in any single experiment.

Another limitation that may be more subtle but is equally important is the issue of how RF irradiation can take place *while* the signal is being received.

The RF receiver is a high sensitivity device designed to record very weak signals (mV). The RF power applied for decoupling will be much greater and the decoupler RF will produce artifacts if special precautions are not taken – one scheme, named time-sharing is shown below:

