THEORY and INTERPRETATION of ORGANIC SPECTRA

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2D NMR Spectroscopy

To record a normal FT NMR spectrum we apply a pulse to our spin system and record the free induction decay (FID) following the pulse. The spectrum is obtained by Fourier Transform where the time dependent FID is converted to a function of frequency, i.e., an NMR spectrum. 2D NMR spectroscopy records a spectrum as a function of two characteristic times. Many FIDs are recorded as a function of a systematically varied delay time.

The typical two-dimensional NMR experiment has three phases; during the preparation phase the system is allowed to relax; then a 90° pulse is applied and the system is allowed to evolve as a function of a delay time, $t_1$, which can be of the order of milliseconds to seconds; then another 90° pulse is applied and the free induction is recorded as a function of time, $t_2$.

The series of experiments yields an array of data as a function of two times. The array is subjected to two consecutive Fourier transformations, the first giving a series of NMR spectra with different delay times, the second
giving a two-dimensional spectrum as a function of two frequencies, either
two chemical shifts or a chemical shift plus a coupling constant.

The first Fourier transform is applied to the
rows, giving a series of NMR spectra; the
second Fourier transform is applied to the
columns, giving a two-dimensional array.

2D Spectra in which both frequencies are chemical shifts are called
correlation spectra; spectra in which one frequency is a chemical shift
whereas the other is a coupling constant are called J–resolved spectra.
Correlation spectra plotting $^1$H chemical shift vs. $^1$H chemical shift are
called COSY (for COrelation Spectroscopy), those plotting $^1$H chemical
shift vs. $^{13}$C chemical shift are called HETCOR (for HETero COrelation
Spectra). Among J-resolved spectra we differentiate between homonuclear J-
resolved ($^1$H chemical shift vs. $^1$H splitting) and heteronuclear J-resolved spectra ($^{13}$C chemical shift vs. $^1$H splitting).

The data can be plotted in two ways, as a stacked plot (left) or as a contour plot (right). The stacked plot contains a large number of 1D NMR spectra presented as a function of the delay time, $t_1$; for clarity each spectrum is shifted slightly relative to the preceding one. The contour plot contains the peak height information as a series of cross sections through the signals at different heights above the x,y plane, projected into that plane.

COSY Spectra

The 2D spectrum of 1-bromopropane is a simple example of a COSY spectrum.
Identical $^1$H spectra are plotted along the x- and y-axes; in addition a contour plot is shown on the diagonal. The off-diagonal peaks, appearing always in pairs, indicate that the central CH$_2$ group is coupled to the terminal CH$_2$ and CH$_3$ groups. Although this is hardly a surprising conclusion for a system as simple as 1-bromopropane, it illustrates the potential of the technique.

The 2D spectrum of 3-heptanone poses a more real problem because the CH$_2$ groups at C-2 and C-4 are not resolved. The off-diagonal peaks in the 2D spectrum allow an unambiguous assignment of all signals; they show the connectivity of the $^1$H nuclei at C-7 (0.6 ppm), with C-6 (1.0 ppm), with C-5 (1.3 ppm) and with C-4 (2.15 ppm) and also the connectivity of the $^1$H nuclei at C-1 with those at C-2.
Special versions of COSY can differentiate between short-range and long-range interactions, as illustrated below.

A more complex spectrum is shown on the next page; some of the cross peaks are identified whereas others have been left as an exercise for you.
This unknown spectrum gives you an opportunity to practice.
HETCOR

2D spectra plotting $^1$H chemical shift vs. $^{13}$C chemical shift are commonly called HETCOR. For a HETCOR spectrum the pulse sequence is changed relative to that for COSY; during the data acquisition phase broadband decoupling is applied to simplify the $^{13}$C spectrum.

The first HETCOR spectrum to be discussed is that of 1-bromopropane, correlating the three $^1$H multiplets (x axis) with the broadband decoupled $^{13}$C resonances (y axis).
Three off-diagonal peaks indicate the carbons to which the H$_2$ and H$_3$ units are attached. Again, the result is hardly surprising for this simple system, but it shows the potential of the technique.

The spectrum of methyl adamantandione carboxylate presents a more challenging problem, including barely separated $^{13}$C signals and overlapping $^1$H multiplet.
HOMONUCLEAR J-RESOLVED

Homonuclear J-resolved spectra, showing $^1$H chemical shift vs. $^1$H splitting can be displayed in two ways. First, the chemical shift can be displayed including the J-coupling, i.e., as a fully coupled spectrum. Alternatively, the 2D array of data points can be tilted by 45°; the resulting spectrum is the equivalent of a decoupled $^1$H spectrum and the 2D spectrum contains the multiplets as vertical columns.
The following 2D spectrum combines a COSY and a fully coupled J-resolved spectrum.
The 2D spectrum of butyl ethyl ether shows both the fully coupled and the decoupled $^1$H spectrum; the 2D data array has been tilted by 45°.
HETERONUCLEAR J-RESOLVED

Heteronuclear J-resolved spectra display $^{13}$C chemical shifts vs. $^1$H splitting; these spectra provide another way to determine the number of $^1$H nuclei attached to a carbon. Our first example shows the heteronuclear J-resolved spectrum of 4-methylpyrimidine. The methyl carbon and the tertiary carbon are clearly discernible from the secondary ones.
A more complex spectrum is shown below as a contour plot and, on the next page as a stacked plot.