7.2: Theory

> **◐ Learning Objectives**
>
> - Learn the difference between 1-D and 2-D NMR spectroscopy

In 1971, Jean Jeener introduced the two dimensional variation of NMR spectroscopy. Since then, scientists have applied the concept to develop the many techniques of two-dimensional (2-D) NMR. Correlation itself is not a new concept in NMR. In ^{1}H NMR spectroscopy, the splitting of resonances indicates that groups were "correlated" to each other due to the spins within each group. Spin-spin splitting gives information about the neighboring nuclei and in the case of ^{1}H NMR, it was how many neighboring hydrogens there were in the molecule. This coupling of hydrogens will be one type of coupling 2-D NMR will consider. The use of 2-D NMR allows for better resolution in signals that normally overlap in 1-D NMR.

All the basic NMR theory for 1-D NMR still applies. In 1-D Fourier transform NMR, a magnetic field is applied to a sample, which is then hit with a series of pulsed radiofrequency (rf), as seen in the pulse sequence below. The Fourier transform of the outgoing signal results in a 1-D spectra as a function chemical shift.
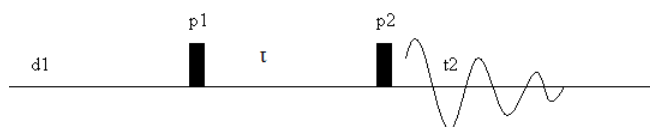
Two-dimensional NMR adds additional experimental variables and thus introducing a second dimension to the resulting spectrum. A simple 2-D experiment pulse sequence consists of a relaxation delay, a pulse, a variable time interval (t_1), a second pulse, and acquisition (t_2). The pulse sequence is repeated many times while varying the length of time (t_1) the system is allowed to evolve during the first pulse. In 2-D experiments, the signal detected during acquisition is a function of acquisition time (t_2), which has been modulated as a function of the time interval (t_1). This means that magnetization evolves around one frequency during t_1 and a different frequency during t_2. The output once Fourier transformed is a 2-D spectrum with two axes. One axis (v_2) represents the nucleus detected during acquisition (t_2), while the other axis (v1) can represent the same nucleus or a different nucleus. With two axes, it leads to cross peaks along a diagonal connecting coupled nuclei. Due to the nature of how the experiment is run, magnetization is redistributed equally in both directions (just like spin-spin coupling), the cross peaks will be symmetrically disposed about the diagonal.

References

Silverstein, R.M, Webster, F.X, and Kiemle D.J. Spectrometric Identification of Organic Compounds. 7th ed. John Wiley & Sons, Inc. 2005.