5 Rotating frame

Larmor nuclear precession frequencies are on the order of tens to hundreds of megahertz. In the electromagnetic spectrum these frequencies reside in the radiofrequency range. Frequencies due to the isotropic chemical shift interaction and other interactions observed in the NMR spectrum are mostly in the audio and ultrasonic frequency range (0-100,000 Hz). Some interactions in solids and paramagnetic systems can be large, rivaling the megahertz frequencies of Larmor precession and cause large second order effects, but these will not be of concern here. Chemical shifts and coupling constants of spin 1/2 nuclei in liquids will be the main topics of this course. These interactions cause small audio frequency modulations of the radiofrequency field. The detection of these small perturbations of the carrier RF field

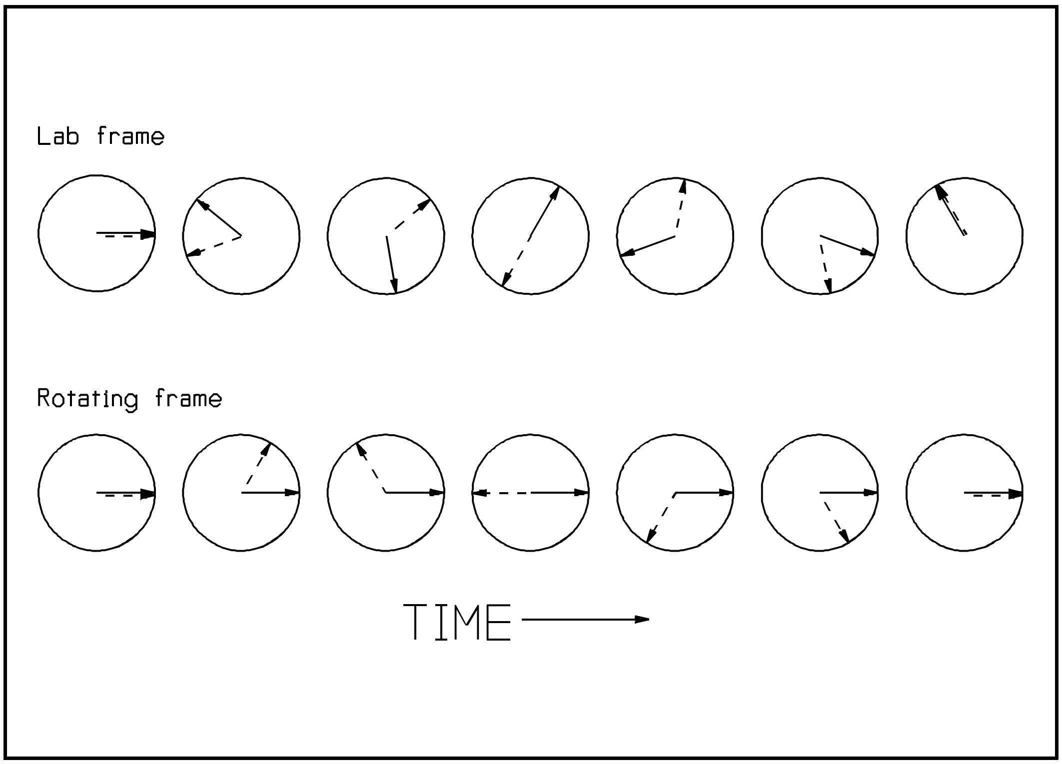

Figure 5.1. Vector picture of two vectors with different frequencies. The top frame is the complicated motion depicted in the laboratory frame and the bottom sequence is depicted in a frame rotating at the frequency of one of the vectors.

is usually carried out by phase sensitive detection. This technique, in effect, subtracts a reference RF frequency, which usually is the excitation (carrier) frequency, from the RF signal containing the audio modulation. The resulting audio frequency is digitized and placed into computer memory for further data processing. All of the interesting information, i.e. the NMR spectrum, is represented by the audio frequency spectrum. In the description of NMR experiments, it is usually convenient to use a mathematical device that eliminates the uninteresting high frequency RF signal and concentrates only on the audio signal which contains the information. This introduces the concept of the rotating frame (Figure 5.1).

The mathematical description of this treatment can be found in almost any basic NMR reference. The description issued here is a merry-go-round. This simple mode nicely describes the rotating frame. A merry-go-round is rotating at a constant frequency with two gnus (vs ?) as passengers. One gnu is standing while the other is walking around the platform in the direction of the rotation but at a velocity that is less than that of the platform rotation. To a third gnu who is grazing in the high field, both gnus on the merry-go-round are moving. The one that is standing on the platform is moving at the rotation velocity of the ride and the one that is walking is moving faster. When the walking gnu turns around and walks the other direction at the same speed, he now appears to move slower than the stationary gnu but still in the same direction since the platform is rotating faster than the gnu is walking. The motion is to complicated for the grazing gnu to bother with so he decides to relax. A spectroscopist, who may be slightly smarter than the gnus, jumps on the ride and thus is transformed into the rotating frame of reference. He now sees a different picture of the gnus. One is moving, either clockwise or counterclockwise at one speed, and the other is still. In the rotating frame the relative motion of the gnus is considerably simplified.

The use of the rotating frame of reference also simplifies the relative motion of nuclear spins and will be used throughout this course unless otherwise stated. In Figure 1 is a comparison of the relative motion of two vectors in the laboratory and rotating frames. In the top figure, the frame is rotating at 2.3 times faster than the two vectors are separating. The relative velocity of the frame to the separation of two spin vectors in NMR is of the order of 10^8. Obviously, the transformation into the rotating frame simplifies the relative motion. The frequency of the rotating frame is generally assigned to the carrier (excitation) frequency so that a resonance that has the same frequency as the carrier frequency will appear to have zero frequency and its representative vector will be stationary. For resonances with frequencies less than the carrier frequency (negative frequencies), the vector that represents the spin will move clockwise in the XY plane as viewed from the positive Z axis. For those with frequencies greater (positive frequencies) than the carrier, the vector will move counterclockwise.

The rotating frame concept can also be generalized to multiple rotating reference frames. This becomes useful in describing the motions of two or more different nuclei (e.g. ^{1}H and ^{13}C) with large differences in their Larmor precession frequencies. Each spin would be referenced to a frame rotating at or near the Larmor precession for that particular spin. The relative motions of the ^{1}H and ^{13}C spins are then much simplified. It must be emphasized that the rotating frame introduces no compromises in the accuracy of the description of the motions of the spins.