

2.2: Measurement of Chemical Shift

Chemical shifts can be measured in several ways. It is quite simple to use an internal standard such as is provided by a sharp resonance line from a solvent or added solute. However, a number of investigations have indicated that internal standards must be used with some care because of possible specific solvent effects and the like. In the final analysis, the best comparisons will be of chemical shifts determined as a function of concentration in a given solvent and extrapolated to infinite dilution. However, this procedure is time consuming, particularly since there is no one solvent which is useful for all types of organic molecules. The special advantage of internal standards as an aid to rapid qualitative analysis of functional groups will be discussed later.

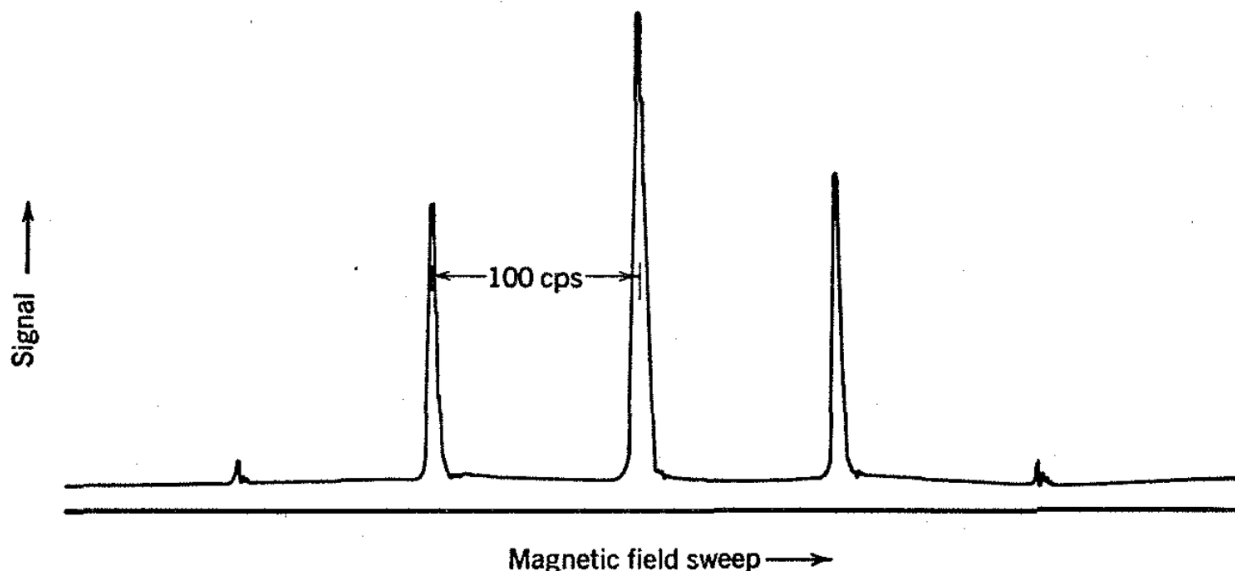


Fig. 2-2. Proton resonance spectrum of benzene at 40 Mc with 100-cps audio frequency superimposed.

Chemical shifts can be conveniently measured relative to an external standard by using a set of concentric tubes, the standard occupying one compartment and the substance under investigation the other. The separation between the standard and sample resonance lines can be taken directly off the recorder chart if the magnetic field sweep is highly stable and linear. Such conditions are not often met in practice and it is common to measure line separations by the audio-oscillator beat method.¹ To do this, one superimposes an audio frequency on the oscillator output, so that the sample is subjected to rotating magnetic field vectors corresponding not only to the principal frequency but also to the beat frequencies which are equal to the principal frequency plus or minus integral multiples of the audio frequency. If the audio power is suitably adjusted, the spectrum of a substance with a single resonance line like benzene appears as shown in Fig. 2-2, with the superimposed audio frequency at 100 cps. The positions of the so-called "sidebands" on the principal resonance can be varied by adjustment of the audio frequency so as to coincide with other signals whose positions are to be measured. With a reasonably stable oscillator, line positions can be determined by this method to better than ± 1 cps. For crude measurements of line positions, it often suffices to use a substitution method in which the sweep rate is fixed, and when the desired resonance is observed, the sample is quickly removed and a standard is inserted with a resonance which falls fairly close to the one that is to be measured.

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