## 4.2: Relationship between Resonance Line Shapes and Exchange Rates

In general, there will be a gradual change in the appearance of a resonance due to a magnetic nucleus in a particular chemical environment as the mean lifetime in that environment decreases. The changes which take place for the simple case where one type of nucleus undergoes exchange between environments A and B, in which on the average it spends equal lengths of time, are shown in Fig. 4-3. When the mean lifetime before exchange ($\tau$A or $\tau$B) is long compared with the transition time between the magnetic energy states, two separate sharp resonances $\delta_{AB}$H apart are observed. When $\tau$A is short compared with the transition times, a single sharp resonance line at 1/2 ($\delta_A$H + $\delta_B$H) is observed. An intermediate broad line is obtained when the mean lifetime before exchange is comparable with the transition time.

Gutowsky[2] has shown that the point at which the separate lines just coalesce corresponds to $\tau$A equal to $\sqrt{2}(\pi\delta_{AB}H)^{-1}$ sec when ( $\delta_{AB}$H) is expressed in cycles per second or $2\sqrt{2}(\pi\delta_{AB}H)^{-1}$ when ($\delta_{AB}$H) is expressed in radians per second. The rate constant in either direction for A $\rightleftharpoons$ B will then be l/$\tau$A. Expressions have also been derived for determining rate constants from changes in resonance line shape. In some instances, rate constants accurate to a few per cent have been reported.

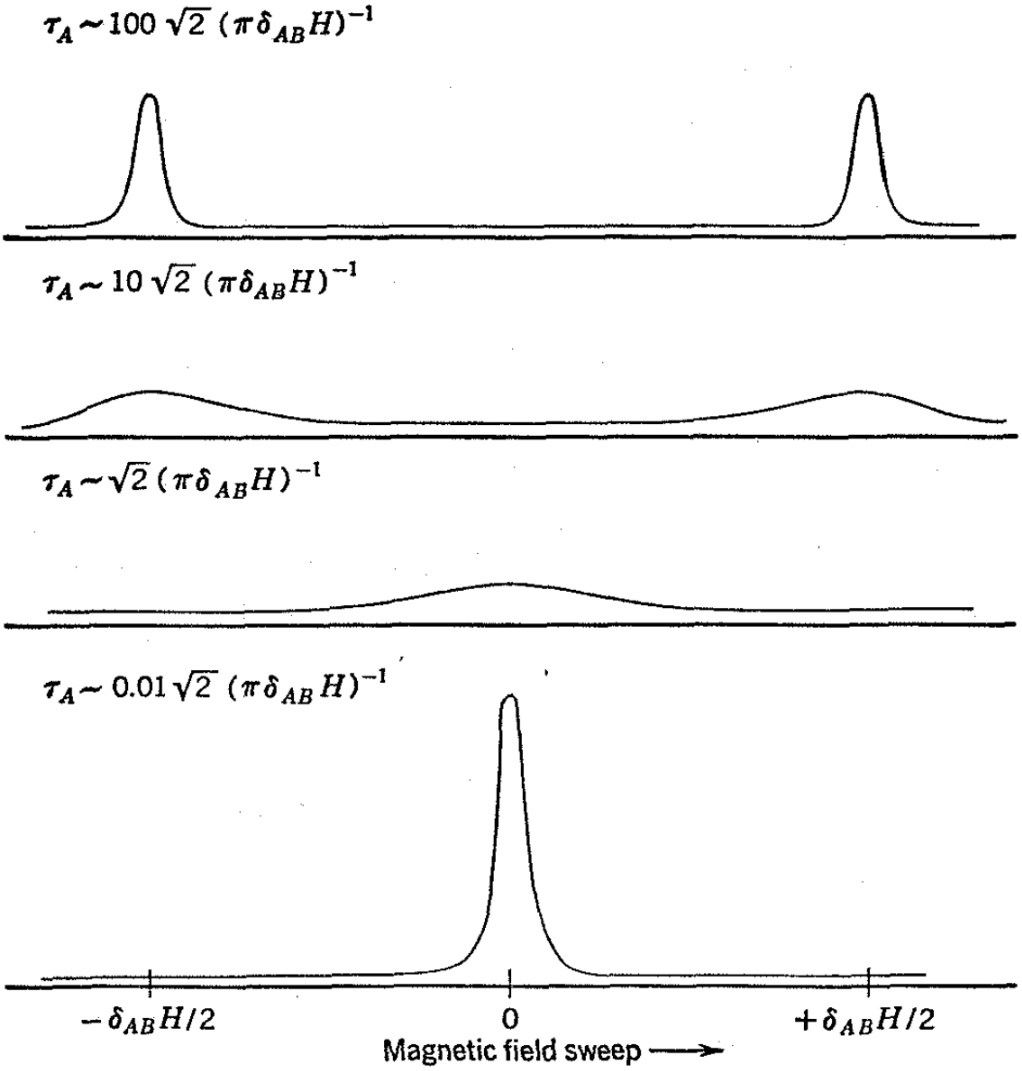


**Fig. 4-3.** Schematic representation of changes of resonance line shapes for protons exchanging between the nonequivalent magnetic environments *A* and *B*, where $[A]/[B] = 1$, as a function of exchange rate. (*Courtesy of H. S. Gutowsky and the Journal of Chemical Physics.*)

Since the easily measurable proton chemical shifts range from 5 to several hundred cycles per second, NMR spectroscopy is most useful for study of reactions which have mean lifetimes of the reacting species ranging between 0.1 and 0.0005 sec. We shall illustrate some of the potentialities of this method of determining reaction rates in a number of different kinds of kinetic processes.

2 H. S. Gutowsky and C. H. Holm, I. Chem. Phys., 25, 1228 (1957).