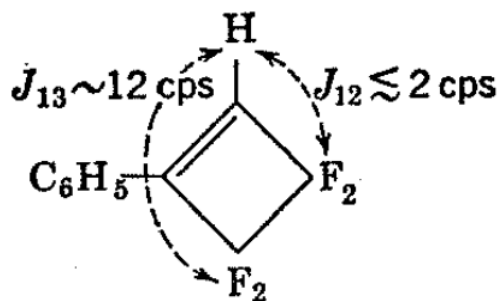


3.3: Spin-Spin Splitting in Liquids

If our hypothetical single crystal of H-D molecules were allowed to melt, the restraints between the molecules would diminish and rapid molecular tumbling would begin. Tumbling molecules present all possible values of the angle θ between the internuclear lines and the magnetic field axis. Integration of $(3\cos^2\theta-1)$ over all possible values of θ shows that the time-average direct dipole-dipole interaction between the bonded H-D nuclei is zero. Hence, we would expect that there would then be no observable spin-spin coupling in nuclear resonance spectra of liquids or gases. Nonetheless, small couplings persist even when tumbling is rapid, although they are usually on the order of about 10^{-2} gauss, roughly 1/1000 of the values expected for direct dipole-dipole interactions. The residual couplings are not merely due to partial averaging of the dipole-dipole interaction through tumbling, since they are temperature independent except in special cases. It has been shown that the residual couplings are the result of magnetic interactions transmitted between nuclei by the bonding electrons in such a way as not to be averaged to zero by tumbling.

Except that the lines are much narrower and very much more closely spaced, the appearance of the NMR spectrum given by tumbling H-D molecules is qualitatively the same as predicted for the single crystal, i.e., a doublet deuteron resonance and a triplet proton resonance. The argument for expecting this pattern is unchanged from that given earlier for the crystal except that now the influence of the magnetic orientation of one nucleus on the precession frequency of the other nucleus is considered to be transmitted by the bonding electrons instead of by direct dipole-dipole interaction.

Gutowsky, McCall, and Slichter¹ discuss the relation between the magnitudes of spin-spin interactions among nuclei as a function of various atomic and molecular parameters. Customarily, spin-spin coupling constants are found to decrease monotonically with the number of chemical bonds between the nuclei involved. Several spectacular failures of this generalization have been observed involving fluorine-fluorine and hydrogen-fluorine interactions. For example, it has been found that the coupling between hydrogen and fluorine atoms connected to the 1 and 3 carbons of certain cyclobutene derivatives, and thus four chemical bonds apart, are much larger than the corresponding interactions between the same groups attached to the 1 and 4 carbons, which are only three bonds apart.² Similarly, the hydrogens on the 1 and 3 carbons of bromoallene (four bonds apart) are coupled more strongly even than the CH₂ and CH₃ hydrogens of an ethyl group (three bonds apart).



¹ H. S. Gutowsky, D. W. McCall, and C. P. Slichter, I. Chem. Phys., 21, 279 (1953).

² C. M. Sharts and J. D. Roberts, I. Am. Chem. Soc., 79, 1008 (1957).

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