Proton Spin Relaxation in Paramagnetic Ion Solutions: Deuterium Isotope Effect

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In aqueous paramagnetic ion solutions the observed rate of proton spin relaxation (1/T2) is controlled by the rate of relaxation in the primary hydration shell of the paramagnetic ion (1/T2e), and by the rate of proton exchange between the hydration shell and the solvent. The relaxation rate is given by

\[\frac{1}{T_2} = P(T_{2e} + \tau_{wx})^{-1}, \tag{1}\]

where \(P\) is the fraction of protons in hydration shells, and \(\tau_{wx}\) is the mean lifetime of a proton in the hydration shell. The effects of isotopic substitution have been studied by measurement of deuteron spin relaxation in D2O solutions \(^1\), \(^2\), and of proton and deuteron relaxation in solutions of mixed isotopic composition \(^3\) — \(^6\). The present discussion will apply to cases like Cr\(^{3+}\) and VO\(^{2+}\), where the dominant exchange mechanism is proton transfer across hydrogen bonds, rather than exchange of whole water molecules. We seek to account for changes in the \(T_2\) of protons (and deuterons) with variation in the isotopic composition of the solution, as have been observed by Mazitov and Rivkind \(^5\), \(^6\).

If the solution contains a mixture of the isotopes \(H\) and \(D\), the factor \(P\) in Eq. (1) is given by

\[P = (n_x/w) (\beta_x/\beta_w), \tag{2}\]

where \(n\) is the hydration number, \(x\) is the paramagnetic ion concentration, \(w\) is the concentration of water molecules, and \(\beta\) is the fractional concentration of protons — i.e., \(\beta_x = H_x/(H_x + D_x)\), and \(\beta_w = H_w/(H_w + D_w)\). Due to the difference in zero-point vibrational energy, the chemical rate constants for H and D exchange dif-

\(^1\) G. Lauckien and F. Noack, Z. Physik 159, 311 [1960].