

## **Dynamics in Proteins from 10 kHz to GHz**

J.-P. Korb, G. Diakova, Y. Goddard, S. Salido, R. G. Bryant\*

Chemistry Department, University of Virginia, Charlottesville, VA 22904 USA  
Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, France

The magnetic field dependence of the proton nuclear spin-lattice relaxation rate (MRD) reports structural fluctuations that modulate proton-proton dipolar couplings. Proton spin-spin communication in the immobilized protein is very rapid; therefore, motion in one region relaxes all protons and the proton MRD provides a global report of protein structural dynamics in the frequency range from 10 kHz to the highest Larmor frequencies achievable in currently accessible magnets. At Larmor frequencies below about 10 MHz, the proton spin-lattice relaxation rate decreases with increasing Larmor frequency according to a power law. We have proposed an original spin-relaxation theory that relates such a frequency variation to the modulation of the proton-proton dipolar couplings and consequently to the molecular motions. This theory is based on a spin-phonon coupling, a normal mode expansion for the structural displacements in the protein, the localization of the structural disturbances, and the spatial distribution of hydrogen atoms in the structure. The success of the theory shows that, although the protons move in 3-dimensions, the propagation of structural disturbance is characterized by a spectral dimension of 1.33 which means that the propagation is approximately 1-dimensional. That is, the structural disturbance is transmitted along the stiff covalent connections of the polypeptide chain, not through the soft potentials of the side-chain interactions in the folded structure. This relaxation mechanism has been successfully tested over the temperature range from 150 K to 310 K and water contents from 0% to full saturation. In hydrated systems, the effects of magnetic coupling between the solid and liquid spins must be taken into account, but the underlying long wavelength protein dynamics control the relaxation processes below a few MHz. At higher Larmor frequencies, the water dynamics at the water-protein interface dominates the proton relaxation processes. The magnetic field dependence of the water-proton spin relaxation rate may be directly related to the distribution of local reorientational motions experienced by the water at the protein surface. The high field MRD provides a map of the surface reorientational correlation time distribution. The data also provide the distribution function for the activation barriers governing the surface dynamics. These measurements show clearly that the dynamical distribution is strongly peaked in the very short correlation time limit. In short, the predominant motions of water molecules in the protein interfacial environment are very rapid in the range from tens of ps.