14.3 Nuclear magnetic resonance (NMR) spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy has become a very powerful and informative technique in a large variety of disciplines of natural science, reaching from solid state physics to mineralogy, all brandches of chemistry, biochemistry, biology, and medicine. NMR takes advantage of the presence of nuclear magnetic moments that interact very weakly with the surroundings but are nevertheless very sensitive to the local environment. This distinguishes NMR from other structural-analytical techniques that explore more global properties, such as ultraviolet spectroscopy observing the electronic excitation of entire molecules, or vibrational spectroscopy measuring the normal vibrational modes of molecules. NMR can, with its numerous "spies", obtain very detailed, highly localized information on molecules and materials. On the other hand, this short sightedness of NMR is a disadvantage when long-range order must be studied. For these investigations, scattering techniques, such as X-ray, neutron and light scattering, can be used.

That the "short-sighted" NMR method could be useful even for the study of anatomical and functional features of the human body is rather unexpected. The crucial concept is the use of an inhomogeneous magnetic field for the encoding of spatial information in the form of shifted resonance frequencies that are proportional to the local magnetic field strength. This leads to *magnetic resonance imaging (MRI)*, a procedure that has significantly enriched non-invasive medical diagnosis. In addition, it is also possible to perform functional studies within a living object, in the form of in-vivo magnetic resonance spectroscopy (MRS). These exciting applications of NMR shall not be further discussed here. The main emphasis is on molecular science.

The determination of the three-dimensional structure of a biomolecule by NMR spectroscopy has become a standard procedure. Geometric information is obtained from the magnetic dipolar interaction that is strictly internuclear-distance dependent and can be determined through the measurement of cross-relaxation rates. In addition, three-bond scalar J_{kl} spin-spin interactions are related to the dihedral bond angles of H_k-C-C-H_l or H_k-N-C-H_l fragments. Based on these two information sources, and taking into account additional constraints given by van der Waals radii and bond-angle limitations, it is possible to determine most feasible molecular conformations. Several computer-based approaches are known iteratively to reach this goal. The most successful procedures are the distance geometry algorithm and restrained molecular dynamics. The resulting structures are normally presented in the form of superimposed families of optimized structures.

Most essential and critical part of the work is the measurement of the basic data, the cross-relaxation rate constants and the *J-coupling constants*. It requires the use of multidimensional spectroscopy. Concerning the fundamental principle of NMR spectroscopy see Section 17.7.6.