

Abstract: This thesis is based on research carried out in different fields ranging from NMR spectroscopy to bonding theory, vibrational spectroscopy, reaction mechanism, and reaction dynamics. A major part of this thesis is devoted to the analysis of indirect scalar NMR spin-spin coupling constants (SSCC) and their four Ramsey terms (FC, DSO, PSO, and SD). The JOC-PSP method was developed to decompose the SSCC into one- and two-orbital terms possessing a clear physical meaning. Using JOC-PSP it was possible to demonstrate the important role of electron lone pairs, which counteract the role of bonding electron pairs in the spin-spin coupling mechanism. Sign and magnitude of each orbital contribution to the four Ramsey terms as well as the total SSCC can be rationalized with the help of first order orbitals and the Fermi contact spin density distribution. In this way the SSCC $^1K(XH)$ for twelve different X atoms from three periods of the periodic table could be explained in detail. The phenomenon of multipath coupling, which makes the interpretation of measured SSCCs of cyclic systems difficult, was also explained in this thesis. - A new NMR-based method for the conformational analysis of pseudorotating rings was worked out, which combines calculated and measured SSCCs. It utilizes generalized Karplus relationships developed in this thesis, which describe the dependence of each SSCC on the puckering coordinates of a ring molecule in form of multidimensional SSCC-hypersurfaces. By combination of the measured SSCCs of a substituted ring system and the calculated generalized Karplus relationships for the corresponding parent ring molecule, a conformational probability distribution can be determined for the substituted system. Using the procedures worked out in this thesis, pseudorotation in cyclopentane, tetrahydrofuran, ribofuranose, and several of their derivatives could be described in detail. - With the help of calculated SSCCs, H-bonding in general and in particular in the protein ubiquitin was investigated and described. A clear answer with regard to the nature of the H-bond could be given. - In general, it is difficult to describe properties of the chemical bond such as covalent character or bond strength with the help of spectroscopic parameters. In this thesis it was shown that the adiabatic force constants are best suited for this purpose, but they lead to the intrinsic bond dissociation energy rather than directly to the bond energy. In general, vibrational spectroscopy is best suited to unravel the electronic and bond structure of a molecule. For this purpose, methods for an automated correlation of vibrational spectra were developed. Spectra correlation relates the electronic structure of one molecule to that of another where these molecules may be structurally related or connected by a reaction path. - The latter situation leads to description of reaction dynamics and reaction mechanism as provided by the unified reaction valley approach (URVA), which was applied in this thesis to investigate mechanistic and dynamic differences between symmetry-allowed and symmetry-forbidding reactions. These studies were highlighted by the discovery of hidden intermediates, the description of the unique role of van der Waals complexes, and an assessment of the dynamic reality of the Woodward-Hoffmann rules. As a more practical example for a mechanistic study, the ozonation of alcohols was investigated in this thesis. This led to the discovery of the important role of trioxides in ozone reactions and the necessity to identify these species with the help of ^{17}O NMR spectroscopy.