STUDIES OF BIOMOLECULES AND THEIR COMPLEXES 
BY NUCLEAR MAGNETIC RELAXATION

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Many biochemical processes, which are essential for life, are dependent on the 
information transfer between the biomolecules which occurs via conformational changes. It is 
believed that intramolecular motions are one of the most important factors which determine 
basic physico-chemical properties, biological activity, and also interactions among 
biomolecules. Nuclear magnetic relaxation is a unique experimental method giving insight 
into dynamic processes existing in biomolecules and covering a broad range of time scales. 
Since most of biomolecules tumble slowly enough to be outside the extreme narrowing region 
the multiple field studies are of great importance.

Oligosaccharides: lactose and fucosyllactoses - $^{13}$C study

Overall and internal motions of lactose and its three fucosylated derivatives were 
studied using relaxation data of $^{13}$C nuclei at two magnetic fields. The relaxation data of the 
inger carbons in calctose and lactosyl core of its derivatives were well described by the axially 
symmetric motion of the molecule. However, a bistable jump model of internal motion was 
required to interpret relaxation data in fucose residues [1].

Supramolecular complexes: cyclodextrins and their complexes - $^{13}$C and $^1$H study

Cyclodextrins, CDs, are macrocyclic oligosaccharides composed of 6-, 7-, 8- or more 
glucopyranoside units. The interest in CD is triggered by their theoretical importance as 
enzyme models on one hand and by their numerous practical applications, in particular, in the 
pharmaceutical industry as drug carriers since CD containers solubilize and stabilize included 
drugs. CDs are chiral. As such, they exhibit chiral recognition, i.e., they differentiate 
enantiomeric species, forming diastereomeric complexes [2].

$^{13}$C nuclear spin relaxation processes in seven subsequent cyclodextrins (from six-
membered $\alpha$ to twelve-membered $\eta$) were investigated at three magnetic fields. The internal 
dynamics in $\alpha$-CD and $\beta$-CD seem to be faster than the overall molecular tumbling, while for 
higher CDs the opposite is true.

1:2 complexes of camphor enantiomers with $\alpha$-CD in $^2$H$_2$O manifested differences in 
longitudinal and transverse relaxation rates of camphor methyl protons owing to chiral 
recognition [3]. The relaxation data obtained at two magnetic fields were quantitatively 
analyzed using the model of anisotropic overall tumbling with internal motion. Anisotropic 
tumbling of camphor molecules provided information on the orientation of the guest in the 
host capsule that for the complex under study could not be obtained by other methods [4].

Protein backbone dynamics - $^{15}$N study

NMR spectroscopy combined with isotopic labeling provides access to NMR 
parameters of almost every atom in a protein molecule. In turn, many of the NMR derived 
parameters are sensitive to protein dynamics. Magnetic relaxation of $^{15}$N amide nuclei allows 
to monitor motions of protein backbone within the wide range of timescales from picoseconds 
to seconds. This approach of probing dynamics of N–H groups allows characterization of 
motions over most of the protein backbone [5].

The ribosome-associated cold shock response protein Yfia of Escherichia coli in the 
free state is built up of two structural segments, a rigid N-terminal part and a flexible C-
terminal tail. The backbone dynamics of Yfia protein was studied by $^{15}$N nuclear magnetic 
relaxation at three magnetic fields and analyzed using model-free approach. The backbone
dynamics of Yfia protein is strongly diversified. The overall tumbling of the rigid N-terminal part comprising 91 amino acid residues is typical for native proteins, whereas the intense local motions within the C-terminal part (22 amino acid residues) are characteristic for the unstructured or denatured proteins. A simultaneous appearance of so different dynamic behaviours in the same protein molecule is very unusual [6].

The PinA protein from the psychrophilic archaeon *Cenarchaeum symbiosum* (PinA) is the first described parvulin-like peptidyl-prolyl isomerase from the archaeal Kingdom responsible for important biological processes. The global and local backbone dynamics of PinA were determined by $^{15}$N nuclear magnetic relaxation at two magnetic fields. The structure of PinA is relatively rigid; only one stretch of residues comprising $\beta_10$-helix III and the following turn displayed significant mobility in the micro- to millisecond time scale. On the other hand, these residues were the most affected by ligand binding pointing out to the catalytic site usually identified basing on the increased local dynamics [7].

S100A1 belongs to EF-hand superfamily of calcium binding proteins. It can be treated as a representative of the S100 protein family because of its amino acid sequence, three-dimensional structure, and biological function as a calcium signal transmitter. It is a homodimer of noncovalently bound subunits. Magnetic relaxation of backbone $^{15}$N amide nuclei of human S100A1 protein was studied at three magnetic fields and analyzed using model-free approach. Dynamics behaviour of three forms of S100A1, calcium-free, calcium-loaded and thionylated at unique cysteine residue, were compared in terms of structural changes induced by calcium binding and thionylation [8,9].

References