

Guest Editorial: NMR Spectroscopy of Hydrogen-Bonded Systems

Since the early years of NMR spectroscopy, this technique has been used to study hydrogen transfer and bonding, which are elementary phenomena important in nature. The NMR interactions exploited were mainly chemical shifts and scalar couplings, but also dynamic effects such as lineshape changes and relaxation gave interesting information. Handicaps of NMR were and often still are the limited dynamic range, which make studies of proton and hydrogen bond exchange difficult. However, in recent decades, more-dimensional multinuclear NMR has made tremendous progress in the study of solids, liquid–solid hybrid systems, soft matter, biomolecules and living systems. Quantum-mechanical computational techniques allow us today to predict NMR parameters with high precision. Hence it is not surprising—although not well known—that because of its high selectivity, NMR plays an increasing role in hydrogen bond research of a growing number of complex systems. Improved techniques are currently used to study not only the structure but also the function and the dynamics of hydrogen bonded systems, ranging from simple molecules to enzymes. On the other hand, the new **Hydrogen Bond NMR** becomes a motor for the development of NMR techniques.

The scope of this Special Issue of *Magnetic Resonance in Chemistry* is to provide in a series of 24 experimental and theoretical papers some snapshots of **Hydrogen Bond NMR**. The issue starts in Section A with a series of papers concerning the ‘Structure and Dynamics of Hydrogen Bonded Solids.’ Here, especially dipolar NH and ND couplings of biological model systems are studied and related to the world of chemical shifts. Such isotope effects provide interesting insights into the proton potentials. They can arise both from anharmonic proton motions and from isotope effects on tautomeric equilibria. The latter can be detected by high-resolution solid-state NMR. The dynamics of protons and deuterons in cyclic hydrogen bonded systems and hydrogen bonded chains can be studied using solid-state longitudinal relaxometry up to the micro- and nanosecond time-scale, as in solids interference with molecular reorientations, generally does not occur.

The next series of papers, in Section B, are devoted to the ‘Structure and Dynamics of Systems with Single Hydrogen Bonds in the Liquid State.’ The problem of the localization and transfer of the proton in acid–base complexes is studied by a combination of chemical shift and relaxometry, and in the case of intramolecular complexes by the measurement of deuterium isotope effects on ^{13}C and ^{15}N chemical shifts. An important task is to elucidate the origin of these hydrogen bond isotope effects, which are strongly influenced by the solvent. Using novel low-temperature NMR methods where deuterated gases are employed as NMR solvents, the regime of slow hydrogen bond exchange can be reached such that different hydrogen bonded species can be distinguished and the effect of dimerization on the hydrogen bond structure studied. In this regime, also intrinsic primary and secondary H/D isotope effects, the effect of the solvent polarity and novel scalar couplings across hydrogen bonds are observed. Two papers, an experimental and a theoretical one, are devoted to the relation between $J(^1\text{H},^{15}\text{N})$ and $J(^{15}\text{N},^{15}\text{N})$ coupling constants and the geometry of NHN hydrogen bonds. Finally, $J(^1\text{H},^1\text{H})$ couplings across hydrogen bonds are calculated in order to detect intramolecular hydrogen bonding in carbohydrates.

The complexity of the systems is increased in the papers in Section C on ‘Hydrogen Bonding in Molecular Liquids and Mesoporous Systems.’ For a molecular hydrogen bonded liquid such as *N*-methylacetamide correlations between structural, NMR and IR spectroscopic properties are calculated and compared with experiments. The interplay between hydrogen bonding and hydrophilicity affects the reorientational dynamics in solution. When chemical shifts do not allow us to determine association, chemical shift resolved diffusion coefficient measurements (DOSY) give interesting insights into the nature of hydrogen bonded complexes. Diffusion coefficient measurements also reveal the effects of hydrogen bonding of pyridine with surface OH groups in the inner pores of mesoporous silica.

The final series of papers, in Section D, are devoted to the study of ‘Hydrogen Bonds in Biomolecules.’ Model systems are developed in order to study substituent effects on the N—H···N hydrogen bonds in duplex DNA and the new field of scalar couplings across hydrogen bonds in these types of molecules is reviewed. A novel technique is proposed to obtain such couplings via ^1H – ^1H correlated spectroscopy. Another new field is the study of C—H···O hydrogen bond interactions in DNA. Using low-temperature NMR techniques, hydrogen bonding in complexes of modified adenosine and 4-thiouridine complexes can be studied. *Ab initio* computational methods are now so much advanced that they can be applied to reproduce

the Karplus relations for model peptides. Finally, two contributions review the area of the role of strong hydrogen bonding in model systems and enzymatic complexes as well in the active sites of enzymes such as serine protease.

This issue does not have the ambition to provide a comprehensive description of all activities of **Hydrogen Bond NMR**, but its goal is to promote this interesting field which provides a unique link of quantum chemistry and quantum biology. It remains to thank all contributors who readily accepted my invitation to present results from their laboratories and who thus made this interesting Special Issue possible.









Hans-Heinrich Limbach

Institut für Chemie der Freien Universität
Berlin, Germany

Editorial

Among the variety of chemical bonds, the *hydrogen bond*, which, because of its general structure $X-H \cdots Y$, is also called *hydrogen bridge*, has a unique position because it is much weaker than classical chemical bonds but at the same time has a much broader distribution in both liquids and solids than any other bond. In particular, its role in biochemistry gives the hydrogen bond outstanding importance and has strengthened the interest in its physical and chemical properties. Intriguing questions, e.g. is the hydrogen bond linear?; what is the position of the hydrogen atom?; is the bond static or dynamic?, have motivated much experimental and theoretical research effort. The earliest spectroscopic technique available to the experimentalist was, of course, IR spectroscopy, which is still an important tool today. With the advent of NMR spectroscopy, a powerful new method became available, especially since proton NMR was the dominant technique at the beginning. Over the years, the different NMR techniques have been applied with great success to the study of hydrogen bond phenomena, and the introduction of new and more sophisticated NMR techniques in recent years has produced impressive results. It was therefore desirable to devote a Special Issue to 'NMR Spectroscopy of Hydrogen-Bonded Systems' in order to give an overview of the state of the art. We are most grateful to Professor H.-H. Limbach, one of the leading NMR spectroscopists in this field, for readily accepting our invitation to act as Guest Editor. He was able to attract a large number of renowned authors as contributors and the result is an excellent collection of articles that treat various aspects of the subject. Our thanks go to the Guest Editor and all the authors for their efforts which made this issue possible. As on similar occasions, our Production Department contributed with its skill to the success. I wish our readers interesting and illuminating reading.

H. Günther
Editor-in-Chief

 Wiley InterScience Home Page	 Personal Home Page	 Journal Finder	 Book Finder	 Search Wiley Interscience
Table of Contents	 All	 Online	 Previous	 Next

Online ISSN: 1097-458X Print ISSN: 0749-1581

[Magnetic Resonance in Chemistry](#)

Volume 39, Issue S1, 2001.

 [About this Journal](#)



Articles Available Online in Advance of Print

(**Special Issue:** NMR Spectroscopy of Hydrogen-Bonded Systems. Issue Edited by Hans-Heinrich Limbach.)

Copyright © 2001 John Wiley & Sons, Ltd.

Guest Editorial

S1-S2 **Guest Editorial: NMR Spectroscopy of Hydrogen-Bonded Systems**

Hans-Heinrich Limbach

[Abstract](#) [PDF Full Text](#) (Size: 44K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.952

Editorial

S3 **Editorial**

H. Günther

[Abstract](#) [PDF Full Text](#) (Size: 30K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.963

Structure and Dynamics of Hydrogen-Bonded Solids

S5-S17 **Investigation of an N...H hydrogen bond in a solid benzoxazine dimer by ^1H - ^{15}N NMR correlation techniques under fast magic-angle spinning**

Gillian R. Goward, Ingo Schnell, Steven P. Brown, Hans Wolfgang Spiess, Ho-Dong Kim, Hatsuo Ishida

[Abstract](#) [PDF Full Text](#) (Size: 605K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.931

S18-S29 **$^1\text{H}/^{15}\text{N}$ NMR chemical shielding, dipolar ^{15}N , ^2H coupling and hydrogen bond geometry correlations in a novel series of hydrogen-bonded acid-base complexes of collidine with carboxylic acids**

Phillipe Lorente, Ilja G. Shenderovich, Nikolai S. Golubev, Gleb S. Denisov, Gerd Buntkowsky, Hans-Heinrich Limbach

[Abstract](#) [PDF Full Text](#) (Size: 397K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.946

S30-S36 **N - H bond stretching in histidine complexes: a solid-state NMR study**

Xiang-jin Song, Chad M. Rienstra, Ann E. McDermott

[Abstract](#) [PDF Full Text](#) (Size: 151K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.956

S37-S43 **Proton transfer dynamics and N - H bond lengthening in N - H...N model systems: a solid-state NMR study**

Xiang-jin Song, Ann E. McDermott

[Abstract](#) [PDF Full Text](#) (Size: 173K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.957

S44-S49 **An indication of slowing down of hydrogen atom transfer in isotopically mixed hydrogen bonds of benzoic acid crystals**

Sadamu Takeda, Akihiko Tsuzumitani

[Abstract](#) [PDF Full Text](#) (Size: 151K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.944

S50-S58 **Mechanism of proton conductivity in quasi-one-dimensional hydrogen-bonded crystals**

J. Totz, D. Michel, Yu. N. Ivanov, A. A. Sukhovskiy, I. P. Aleksandrova, J. Petersson

[Abstract](#) [PDF Full Text](#) (Size: 261K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.918

Structure and Dynamics of Systems with Single Hydrogen Bonds in the Liquid State

S59-S66 **NMR properties (chemical shift and relaxation rate) of acceptor and hydrogen bridge nuclei in hydrogen-bonded complexes**

Alessandro Bagno, Enzo Menna, Gianfranco Scorrano, Simonetta Zerbinati

[Abstract](#) [PDF Full Text](#) (Size: 152K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.914

S67-S80 **NMR study of proton transfer equilibrium in Schiff bases derived from 2-hydroxy-1-naphthaldehyde and 1-hydroxy-2-acetonaphthone. Deuterium isotope effects on ¹³C and ¹⁵N chemical shifts**

T. Dziembowska, Z. Rozwadowski, A. Filarowski, P. E. Hansen

[Abstract](#) [PDF Full Text](#) (Size: 173K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.949

S81-S90 **Dimerization and solvent-assisted proton dislocation in the low-barrier hydrogen bond of a Mannich base: a low-temperature NMR study**

Maria Rospenk, Lucjan Sobczyk, Parwin Schah-Mohammedi, Hans-Heinrich Limbach, Nicolai S. Golubev, Sonya M. Melikova

[Abstract](#) [PDF Full Text](#) (Size: 264K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.943

S91-S99 **Influence of the temperature-dependent dielectric constant on the H/D isotope effects on the NMR chemical shifts and the hydrogen bond geometry of the collidine-HF complex in CDF₃/CDCIF₂ solution**

Ilja G. Shenderovich, Andrej P. Burtsev, Gleb S. Denisov, Nikolai S. Golubev, Hans-Heinrich Limbach

[Abstract](#) [PDF Full Text](#) (Size: 316K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.938

S100-S108 **Scalar coupling constants across the intramolecular NHN hydrogen bond of symmetrically and non-symmetrically substituted 6-aminofulvene-1-aldimines**

Mariusz Pietrzak, Hans-Heinrich Limbach, Marta Pérez-Torralba, Dionísia Sanz, Rosa María Claramunt, José Elguero

[Abstract](#) [PDF Full Text](#) (Size: 239K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.937

S109-S114 **^{15}N , ^{15}N spin-spin coupling constants across N - H - N and N - H⁺ - N hydrogen bonds: can coupling constants provide reliable estimates of N - N distances in biomolecules?**

Janet E. Del Bene, S. Ajith Perera, Rodney J. Bartlett

[Abstract](#) [PDF Full Text](#) (Size: 142K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.913

S115-S125

Density functional theory studies of transannular ^1H - ^1H J-coupling in half-cage alcohols and rigid 1,3- and 1,4-diols: conformational dependencies and implications for intramolecular hydrogen bond detection in carbohydrates

Michael Barfield, Jon M. Bergset, Daniel J. O'Leary

[Abstract](#) [PDF Full Text](#) (Size: 429K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.930

Hydrogen Bonding in Molecular Liquids and Mesoporous Systems

S127-S134 **Correlations between structural, NMR and IR spectroscopic properties of N-methylacetamide**

M. Huelsekopf, R. Ludwig

[Abstract](#) [PDF Full Text](#) (Size: 170K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.912

S135-S141 **Reorientational dynamics, hydrogen bonding and hydrophilicity of X-ray contrast agents in solution**

Michael van de Bruck, Andreas Dölle, Günter Michl, Bernd Radüchel

[Abstract](#) [PDF Full Text](#) (Size: 122K)

Published Online: 5 Nov 2001

DOI 10.1002/mrc.936

S142-S148

DOSY studies of hydrogen bond association: tetramethylsilane as a reference compound for diffusion studies

Eurico J. Cabrita, Stefan Berger

[Abstract](#) [PDF Full Text](#) (Size: 132K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.917

S149-S157 **Stray field gradient NMR reveals effects of hydrogen bonding on diffusion coefficients of pyridine in mesoporous silica**

E. Gedat, A. Schreiber, G. H. Findenegg, I. Shenderovich, H.-H. Limbach, G. Buntkowsky

[Abstract](#) [PDF Full Text](#) (Size: 220K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.932

Hydrogen Bonds in Biomolecules

S159-S165 **Developing model systems for the NMR study of substituent effects on the N - H...N hydrogen bond in duplex DNA**

Rei Ishikawa, Chojiro Kojima, Akira Ono, Masatsune Kainosho

[Abstract](#) [PDF Full Text](#) (Size: 167K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.941

S166-S170 **Applications of $^1\text{H}_a$ - $^1\text{H}_d$ correlated $^{2h}\text{J}(\text{N},\text{N})$ spectroscopy for identifying H_a - C - N_a...H_d - N_d hydrogen bonds in nucleic acids**

Ananya Majumdar

[Abstract](#) [PDF Full Text](#) (Size: 255K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.947

S171-S176

Investigation of the energetics of C⁺H...O hydrogen bonds in the DNA i-motif via the equilibrium between alternative intercalation topologies

Jean-Louis Leroy, Karim Snoussi, Maurice Guéron

[Abstract](#) [PDF Full Text](#) (Size: 195K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.935

S177-S182 **Hydrogen bonding in complexes of adenosine and 4-thiouridine: a low-temperature NMR study**

Eline M. Basilio Janke, Anita Dunger, Hans-Heinrich Limbach, Klaus Weisz

[Abstract](#) [PDF Full Text](#) (Size: 144K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.945

S183-S189 **A correlated *ab initio* study of Karplus relations for model peptides**

S. Ajith Perera, Rodney J. Bartlett

[Abstract](#) [PDF Full Text](#) (Size: 148K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.911

S190-S198 **Review: Strong hydrogen bonding in molecules and enzymatic complexes**

Perry A. Frey

[Abstract](#) [PDF Full Text](#) (Size: 168K)

Published Online: 5 Nov 2001

[DOI](#) 10.1002/mrc.953

S199-S213 **Review: Contributions of NMR spectroscopy to the study of hydrogen**

bonds in serine protease active sites

William W. Bachovchin

[Abstract](#) [PDF Full Text](#) (Size: 336K)**Published Online:** 5 Nov 2001**DOI** 10.1002/mrc.951

[\[Wiley InterScience Home Page\]](#) [\[Personal Home Page\]](#) [\[Journal Finder\]](#) [\[Book Finder\]](#) [\[Search Wiley InterScience\]](#)
[\[Reference Works\]](#) [\[Help\]](#) [\[Contact Us\]](#) [\[Logout\]](#)

[Copyright ©](#) 1999-2001 by [John Wiley & Sons, Inc.](#) All rights reserved.