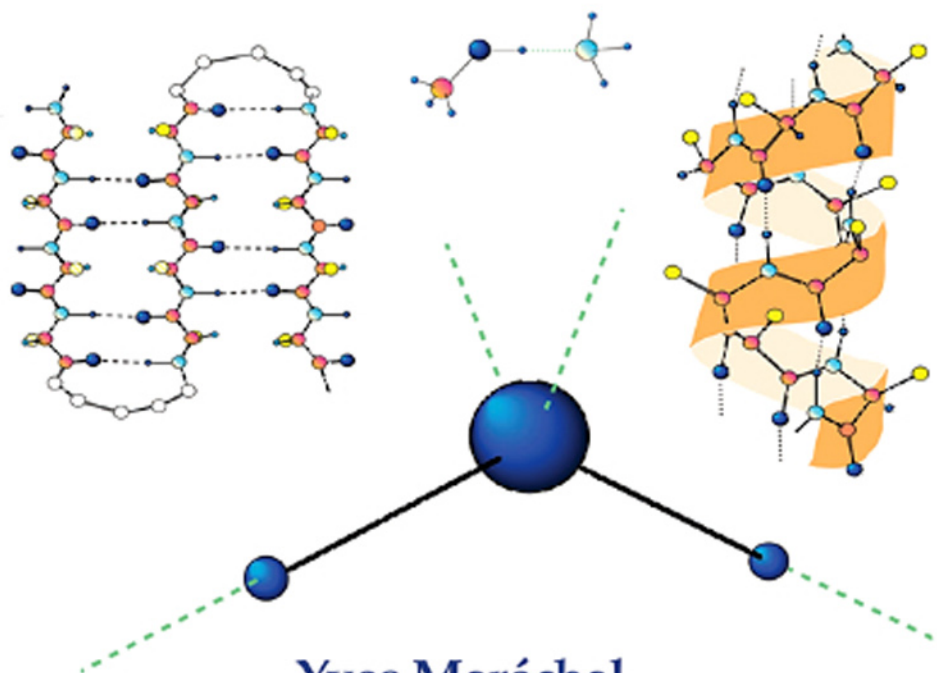
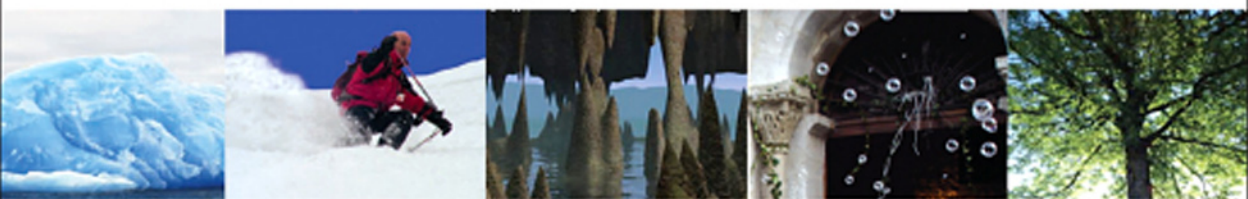


# *The Hydrogen Bond and the Water Molecule*

The physics and chemistry of water, aqueous and bio media



Yves Maréchal

# **The Hydrogen Bond and the Water Molecule**

**The Physics and Chemistry of Water,  
Aqueous and Bio Media**

This page intentionally left blank

# **The Hydrogen Bond and the Water Molecule**

## **The Physics and Chemistry of Water, Aqueous and Bio Media**

Yves Maréchal

*DRFMC/SI3M-CEA*

*Grenoble, France*



ELSEVIER

Amsterdam • Boston • Heidelberg • London • New York • Oxford  
Paris • San Diego • San Francisco • Singapore • Sydney • Tokyo

Elsevier

Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands  
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK

First edition 2007

Copyright © 2007 Elsevier B.V. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: [permissions@elsevier.com](mailto:permissions@elsevier.com). Alternatively you can submit your request online by visiting the Elsevier web site at <http://elsevier.com/locate/permissions>, and selecting *Obtaining permission to use Elsevier material*

#### Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

#### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

#### British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN-13: 978-0-444-51957-3

ISBN-10: 0-444-51957-2

For information on all Elsevier publications  
visit our website at [books.elsevier.com](http://books.elsevier.com)

Printed and bound in Italy

07 08 09 10 11 10 9 8 7 6 5 4 3 2 1

Working together to grow  
libraries in developing countries

[www.elsevier.com](http://www.elsevier.com) | [www.bookaid.org](http://www.bookaid.org) | [www.sabre.org](http://www.sabre.org)

ELSEVIER

BOOK AID  
International

Sabre Foundation

# Contents

<i>Acknowledgments</i> . . . . .	<i>ix</i>
<i>Preface</i> . . . . .	<i>xi</i>

<b>Part I</b>	<b>The Hydrogen Bond</b> . . . . .	<b>1</b>
---------------	------------------------------------	----------

<b>Chapter 1</b>	<b>The Hydrogen Bond: Formation, Thermodynamic Properties, Classification</b> . . . . .	<b>3</b>
	Chemical Bonds . . . . .	3
	Intermolecular Bonds . . . . .	4
	Van der Waals interactions . . . . .	4
	Hydrogen bonds . . . . .	6
	The H-Bond: Historical and Prospective Aspects, General Bibliography . . . . .	7
	Intermolecular and Intramolecular H-Bonds . . . . .	9
	Electronic Structures of Hydrogen Bonds . . . . .	10
	Thermodynamics of H-Bonds: Electronic and Vibrational Contributions to Enthalpies . . . . .	12
	Examples of Weak, Intermediate Strength and Strong H-Bonds . . . . .	16
	Weak H-bonds . . . . .	16
	Medium-strength H-bonds . . . . .	18
	Strong H-bonds . . . . .	19
	Nonconventional H-Bonds . . . . .	19
	H/D Substitutions in H-Bonds . . . . .	21
	Appendix: Energies and Related Quantities . . . . .	22
	References . . . . .	23

<b>Chapter 2</b>	<b>Geometrical Properties of H-Bonds and H-Bonded Organized Supramolecular Structures.</b> . . . .	<b>25</b>
	Geometries of H-Bonds at Equilibrium . . . . .	25
	Equilibrium angles $\theta_0$ and $\varphi_0$ . . . . .	26
	Equilibrium distances $Q_0$ . . . . .	27
	Equilibrium distances $q_0$ . . . . .	29
	Organized Supramolecular Structures of Macromolecules . . . . .	29
	Cellulose and amylose . . . . .	30
	Proteins . . . . .	33
	DNA . . . . .	41
	Conclusion . . . . .	46
	References . . . . .	47

<b>Chapter 3</b>	<b>Methods to Observe and Describe H-Bonds</b>	<b>49</b>
	Calorimetry	49
	Modern Experimental Methods	51
	Absorption of an electromagnetic wave	52
	Scattering of electromagnetic waves or particles	61
	Theoretical Descriptions of the Electronic Structures of H-Bonds	69
	Summary	72
	References	74
 <b>Chapter 4</b>	 <b>Infrared and Related Spectroscopies of H-Bonded Systems:</b>	
	<b>Experimental Point of View</b>	<b>77</b>
	IR Spectroscopy and H-Bond Vibrations	77
	Intermonomer Vibrations in the FIR Region	78
	Description	78
	Anharmonicities of intermonomer modes	81
	Intramonomer Vibrations in the Mid-IR Region	84
	Stretching bands $\nu_s$	85
	Other intramonomer bands	98
	Multiphoton Vibrational Spectroscopies: Raman and Nonlinear IR	105
	Raman spectra	105
	Time-resolved nonlinear IR spectroscopies	106
	Sum-frequency generation spectroscopy	109
	Conclusion	110
	References	111
 <b>Chapter 5</b>	 <b>Infrared Spectroscopy of H-Bonded Systems:</b>	
	<b>Theoretical Descriptions</b>	<b>115</b>
	Introduction	115
	Integrated Intensities of $\nu_s$ Bands	115
	$\nu_s$ Bandshapes of Isolated H-Bonds: Modulation by	
	Intermonomer Modes	116
	Modulation by intermonomer stretching modes	117
	Modulation by intermonomer bending modes	123
	$\nu_s$ Bandshapes of Nonisolated H-Bonds	123
	$\nu_s$ Bandshapes of H-Bonds: Fermi Resonances	124
	Conclusion on $\nu_s$ Bands	128
	Appendix: IR Spectroscopy	128
	Experimental spectroscopy: measured quantities	
	and set-ups	129
	First moments of a distribution or of a spectral band	134
	Normal modes in the harmonic approximation	136
	Reduced masses, force constants and vibrational amplitudes	137
	Centre and width of $\nu_s$	139
	References	144

<b>Chapter 6</b>	<b>Reactivity of Hydrogen Bonds: Transfers of Protons and of H-Atoms</b>	<b>147</b>
	Great Amplitude Motions in Isolated H-Bonds	147
	Proton Transfers in an H-Bond Network	150
	Ionization mechanism of an acid or a base	150
	Diffusion of $\text{H}_3\text{O}^+$ and $\text{O}-\text{H}^-$ ions in liquid water	154
	Proton Transfers in the Electronic Excited State	156
	Photoacids	156
	ESPT's in biology: photosynthesis and vision mechanisms	157
	H-Bonded Ferroelectrics	164
	Hydrogen Atom Transfers by Tautomerism	166
	Conclusion	170
	References	171
<b>Chapter 7</b>	<b>H/D Isotopic Substitution in H-Bonds</b>	<b>173</b>
	The H and D Atoms: Similarities and Differences	173
	Geometries and Thermodynamics of H-Bonds and D-Bonds	174
	Geometries of H-bonds and D-bonds	174
	Enthalpies of H-bonds and D-bonds	176
	Dynamic Properties of H-Bonds and D-Bonds	178
	Vibrational spectra of H-bonds and D-bonds	178
	Partial H/D substitution and isotopic dilution	180
	H/D substitution in biology: a dramatic effect on reactivity	184
	H-Bonds and D-Bonds as seen by Methods Sensitive to Nuclear Spins	185
	Conclusion	186
	Appendix	187
	References	190
<b>Part II</b>	<b>The Water Molecule</b>	<b>193</b>
<b>Chapter 8</b>	<b>The <math>\text{H}_2\text{O}</math> Molecule in Water Vapour and Ice</b>	<b>195</b>
	$\text{H}_2\text{O}$ : An Exceptional Molecule	195
	Water Vapour	197
	The major greenhouse gas and its strong IR bands	197
	Formation of raindrops	199
	Ice (s)	199
	Ice Ih and ice Ic	200
	Other crystalline phases of ice	205
	Ice Ih/liquid water interface	206
	Amorphous phases of ice	207
	Reactivity of ice	208
	Conclusion	211
	References	212



<b>Chapter 9</b>	<b>The H<sub>2</sub>O Molecule in Liquid Water</b>	<b>215</b>
	H-Bonds in Liquid Water	215
	Thermodynamics	216
	IR spectroscopy	216
	Structure of the H-bond network of liquid water	223
	The Exceptional Properties of Liquid Water	224
	Exceptional chemical properties	225
	Exceptional physical properties	238
	Our Understanding of Liquid Water	242
	Conclusion	245
	References	247
<b>Chapter 10</b>	<b>The Water Molecule in (Bio)Macromolecules</b>	<b>249</b>
	Water Molecules and their Dense Hydrogen Bond Networks	249
	Arrangements of Water Molecules in Macromolecules	251
	Hydration mechanisms	251
	Protection of biomacromolecules against external stress (cryo and lyoprotections)	264
	Protein folding	267
	Reactivity of Water Molecules in Macromolecules	268
	Conclusion	273
	References	275
<b>Chapter 11</b>	<b>Observing the Water Molecule</b>	<b>277</b>
	A Difficult-To-Observe Molecule	277
	Global Methods	278
	Classical Molecular Methods Other than Vibrational Spectroscopy	279
	X-ray scattering	279
	Neutron scattering	280
	NMR spectroscopy	283
	Molecular dynamics (MD)	284
	Vibrational Spectroscopy	285
	IR spectroscopy to observe H <sub>2</sub> O molecules	286
	NIR and Raman spectroscopies	300
	Conclusion	301
	References	302
<b>Part III</b>	<b>General Conclusion</b>	<b>305</b>
<b>Chapter 12</b>	<b>Conclusion: H-Bond, Water Molecule and Life</b>	<b>307</b>
<i>Index</i>		<i>311</i>

## Acknowledgments

I am grateful to many persons for the precious aid they provided me during the research activity I had on hydrogen bonds and water molecules and during the writing of this book. First, Andrzej Witkowski under whose direction I started, a long time ago, my thesis on the IR spectra of hydrogen bonds and whose constant questioning on topics of physics and on many other intellectual issues, always revealed original ways of thinking. Then, Hans Rainer Zelsmann, with whom I worked for several decades on hydrogen bonds. Without him and his always highly valuable and rigorous advices I would never have reached anywhere in the interpretations of experiments where they can be considered as fully exploited. I am also grateful to initiators of the hydrogen bond research community, particularly Dusan Hadzi, Camille Sandorfy, Lucjan Sobczyk, Savo Bratos and Henryk Ratajczak, with whom I had numerous and often passionate discussions on hydrogen bonds. Also John E. Bertie, with whom we exchanged views on precise measurements of intensities in IR spectra, a somewhat great number of years ago, and Ludwig Hofacker for offering a fruitful collaboration, an even greater number of years ago.

I would also thank Serge Pérez, who gave me the opportunity to deliver lectures on hydrogen bonds and water molecule in doctoral teachings (Diplome d'Etudes Approfondies) on Physical Chemistry at the Joseph Fourier University in Grenoble. These lectures and corresponding exchanges with Students gave me the idea of writing this book. Before writing it, I particularly benefited from the great experiences in scientific publications of Austin Barnes and Jean Bornarel.

Discussions on special topics evocated in this book allowed me getting a sufficiently precise view of these topics. I particularly thank the following: Philippe Pruzan, who unfortunately passed away much too early, but to whom I am indebted for having sent me diagrams on the various phases of ice and articles on the spectroscopy of ice; André Grand for discussions on DFT methods; Olivier Henri-Rousseau and Paul Blaise for their readings and comments on these central chapters of this book that concern IR spectroscopy of H-bonds; Armel Guillermo, Michel Bardet and Jacques Gaillard for having raised my attention to the advent of recent NMR methods to look at hydrogen bonds and having provided me with related references; and Yoshiharu Nishiyama for references concerning the development of algae in heavy water. Life in heavy water provides a central argument discussed in this book on the fundamental role of water molecules in the bioreactivity; many other persons who did not hesitate sparing time explaining me particular points.

I finally acknowledge the invaluable support provided by my own family, particularly my wife Marie-France, during the long time that this book was written.

This page intentionally left blank

## Preface

In one of his “News and Views” in *Nature* (332 (1988) 677), John Maddox wrote some 20 years ago: “Is the scandal, that so little is known about the interactions of macromolecules and their aqueous environment, about to be removed?” This one sentence clearly defines the aim of this book. What is the point? The water molecule,  $\text{H}_2\text{O}$ , is one of the most familiar molecules. It is the component of a species, liquid water, which we all drink daily and use in many various ways. It is therefore no surprise that  $\text{H}_2\text{O}$  is often considered a “casual” molecule. It nevertheless remains surprising that it is considered at the same time a molecule with almost no interest and which can be consequently ignored. John Maddox called this attitude a scandal, as it is indeed untenable. It actually disregards a fundamental point: life, which started developing some 3–4 billion years ago within the oceans, requires the presence of these molecules to proceed. In other words, we know that in biology this molecule plays a central role and we nevertheless often continue ignoring it. Why is this so, and will it still remain so for long? One of the reasons for this attitude is that the water molecule is much more difficult to observe than currently thought. However, it has been the object of many research activities in various fields in recent years. The development and efficiency of experimental methods that were previously severely hindered when used to observe the water molecule have conveyed new pieces of information, giving evidence of subtle and discrete properties that make it a far more active molecule than previously thought, not only in biology but also in physics and chemistry. As time goes on our knowledge of this molecule and its role thus becomes more and more precise. The aim of this book is our present view of this molecule, in the hope that it is no longer ignored where it intervenes, often decisively and much more often than ordinarily thought, and also in order to clearly show what we still have to learn about it. On reading the conclusion at the end of this book, it should be clear that in recent years our point of view on this molecule has changed fundamentally.

Understanding the subtle properties of the water molecule, which indeed make it an exceptional molecule, requires first having a precise knowledge of the molecular interaction that is at the origin of all its properties: the hydrogen bond (H-bond in this book). An important part of this book, about half of it, is therefore devoted to the properties and implications of this crucial intermolecular bond that many scientists often use and invoke for a particular property of its own without having an overview of all of its properties and implications. The geometrical and thermodynamic properties of the H-bond are well known and have been described in several classical textbooks. They are briefly but precisely reviewed and commented in the first chapters of this book that precede chapters devoted to the experimental and theoretical methods that are particularly adapted to the observation and description of H-bonds. The dynamic properties of H-bonds, at the origin of their particularly crucial reactivity, are examined in a separate chapter. Their fundamental importance has recently emerged, and their study constitutes a field of a growing interest in physics and chemistry. The description of these dynamic properties starts with that of the exceptional features it displays in its vibrational spectra. We shall see that IR spectroscopy appears to be the most

precise tool to observe both H-bonds and the water molecule, an opinion that only specialists have shared until recently. It will also hopefully make it evident that this powerful tool, IR spectroscopy, is not so hard to handle as commonly thought. It should thus help stimulate more scientists to use vibrational spectroscopy with confidence, as it is now well understood. Even if it requires some care in its interpretations, it is no longer a method to be used only by specialists. The introduction of anharmonicity, a concept that naturally explains the exceptional spectroscopic properties of H-bonds, makes it moreover easy to understand how H-bonds are the path through which protons and hydrogen atoms can be transferred between molecules. Some kinds of proton transfers, such as those that are at the origin of all acid/base chemistry, are reasonably well known. Some others, which occur in such biomechanisms as photosynthesis or vision, are the object of intense research activity and are less known. Even less known, however, are transfers of H-atoms via tautomerism, which we now suspect to be crucial mechanisms in enzymatic activity, or more generally to be the basic mechanisms of bioreactivity. In these transfers, water molecules play a crucial role, and at the end of this part devoted to H-bonds, it should clearly appear that if H-bonds are at the origin of nearly all the properties of the water molecule, they could not play the central role they have in chemistry and biology if water molecules did not exist. In other words, H-bonds and water molecules are so intricately linked that they cannot be separated.

In view of the above noted contradictions and paradoxes that the simple-looking and familiar water molecule conveys, and which have only recently been recognized, it is now timely to clarify what we know, what we ignore of this crucial and ubiquitous molecule and of the H-bond which gives it nearly all its properties, and also what questions and/or long-term implications the newly revealed aspects of this molecule raise. One of these questions, a fundamental one already outlined above, is: *how is it that life occurs within water, and within water only?* An older but somewhat vague answer is that water is important in biology to provide a medium for biosystems. In the light of recent studies this answer can be made with much more precision and constitutes a guideline for the whole book. It is: water molecules, with their unique ability to develop a particularly dense, evolutive, and flexible H-bond network, not only influence the structure of many a macromolecule, but, potentially more important, play a crucial role in the reactivity of all bio-media, at neutral pH, by enabling transfers of H-atoms that are now suspected to constitute the elementary reactions in such media. This property comes in addition to the well-known one, which is that in any aqueous system they also enable transfers of protons, the origin of all acid/base chemistry.

Such a book, which attempts to make a synthesis of what is known, what is being studied and what is at stake in a field of research of growing interest (water and aqueous media are ubiquitous; H-bonds are central in molecular biology) has the ambition of being a reference book for various scientists in many different fields of interest, which extend from physics to biology and naturally includes chemistry. It is aimed at collecting from an appreciable part of the whole scientific endeavour and presenting with some unity items of knowledge all related to the water molecule. From another point of view, many scientists in completely different fields often encounter the H-bond or the water molecule in their own domain. They may be eager for more precise knowledge of what they are dealing with in order to place their own field of research in a wider domain. This book is aimed at helping them do so. With this view an appreciable part of the book concerns various methods that can be used to observe different features of H-bonds and of the water molecule. This book

might thus help in defining strategies for many studies where these two entities, the H-bond and the water molecule, are encountered. It should also interest science students who have to learn physical chemistry, biophysics or biochemistry, the physics of the atmosphere, of ice or of this special liquid: water. It might also help instructors lecturing on H-bonds, water molecules and many related domains.

This book has been written with the rigor and criticism that a physicist or a chemist requires. It has also been written in such a way that a biologist should not encounter difficulties reading it, because biology is the field where H-bonds and water molecules show their fundamental and even vital importance. Biologists also require rigor and criticism in their own domains, but the objects they study being different and particularly complex, they do not put the emphasis on the same points. With this in mind, the necessary mathematical developments to describe some particular points are often given in appendices at the end of chapters. When they cannot be avoided in the text, as for instance in the description of the H-bond network of liquid water, which is still presently the object of passionate discussions in the community of chemical physicists, or in the mechanics of H-bonds necessary to understand their IR spectra, a sentence indicates what in the following developments the uninterested reader can skip and where he or she should resume reading. Will it be enough to make this goal of having a book that is intended to be read by such a wide variety of scientists of different cultures viable? No answer can be given at present but the question itself points to the challenge encountered in writing this book.

This page intentionally left blank

# **Part I**

## **THE HYDROGEN BOND**

---



This page intentionally left blank