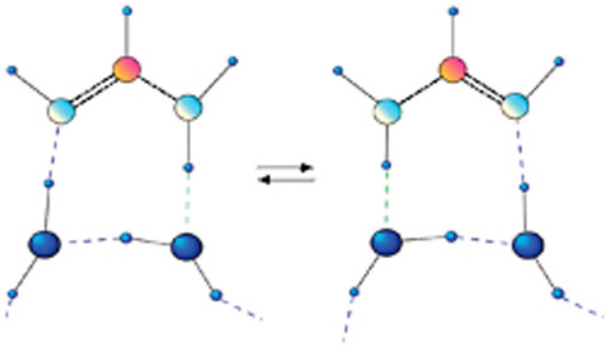
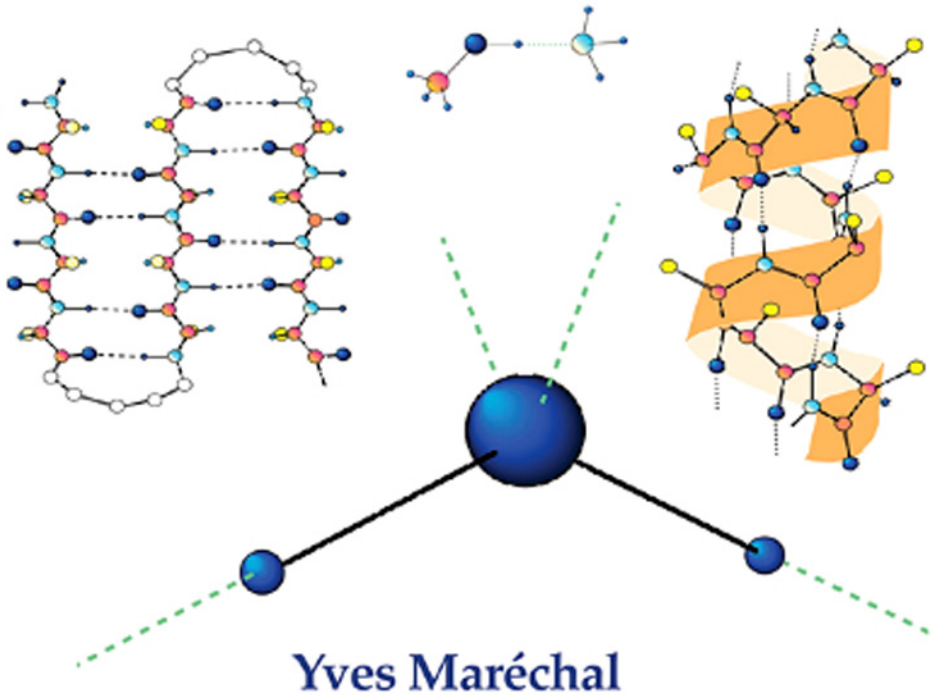


The Hydrogen Bond and the Water Molecule

The physics and chemistry of water, aqueous and bio media



Yves Maréchal

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The Physics and Chemistry of Water, Aqueous and Bio Media

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The Hydrogen Bond and the Water Molecule

The Physics and Chemistry of Water, Aqueous and Bio Media

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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, H_2O, 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 H_2O 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.

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Part I

THE HYDROGEN BOND

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