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## Modeling two-dimensional infrared spectroscopy of hydrogen bonded systems

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# 1

## GENERAL INTRODUCTION

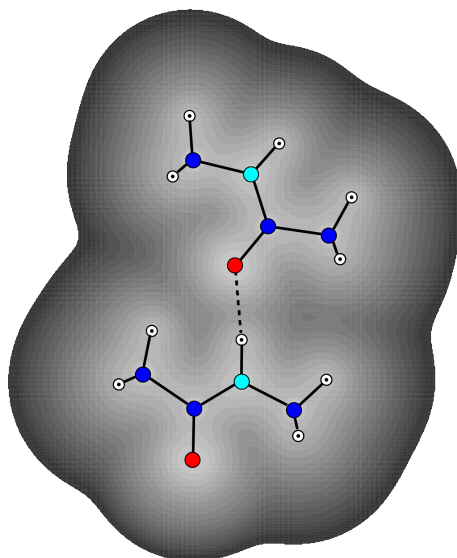
Since the early ages of history the fundamental question: “What is matter composed of?” has been in the mind of people. The answer to this question varied through the years with chemical affinities being described in 1675 by Lemery in the book “*Cours de Chymie*” [1,2] and in 1749 published as affinity data by Pierre-Joseph Macquer [3], in the first volume of his monograph entitled “*Chimie Theorique*”. However, with the atomic hypothesis by Dalton [4] the theory of elective affinity was left aside. At first the atoms were described as elementary particles that composed all the matter, from which the notion of molecules was derived [5]. Through the years all these concepts changed as new discoveries were made and a major step was taken with the discovery of the electron. The notion of atomic structure, a nucleus surrounded by electrons, led to the description of the chemical bond as sharing an electron pair, by Lewis in 1916 [5,6]. The concept of chemical bonding has been refined with time by many other scientists, such as Linus Pauling [7], and huge steps to understand the composition of matter have been taken. But after all: What is chemical bonding?

A chemical bond is a long lived interaction between two atoms, which may arise from sharing electrons (covalent bonding) or from electrostatic interactions between atoms with opposite charges (ionic bonding) [5]. When two neutral atoms share their electrons, a covalent bond is formed. If the electronegativity of the atoms involved in the bonding differs, the bond is polar, and the electrons are not equally shared anymore, resulting in partial charges on the atoms. In the extreme case where the electron is “fully” transferred from one atom to the other, an ionic bond is formed, and the two atoms are held together by electrostatic interactions. The types of chemical bonds may vary from strong (covalent, ionic and metallic bonds) to weak, such as London dispersion forces [8–10] and hydrogen bonds. Thus, the chemical bonds are, not only, the glue that keeps the matter together, but are also responsible for the diversity of structures and materials in nature. For example, metallic bonds are present in metals, covalent bonds (apolar and polar) in organic molecules, while hydrogen bonds constitute the basis of diversity of biological systems. Thus, understanding chemical bonding is a path to deepen our knowledge regarding the structural

and dynamical properties of matter. After all: Do chemical bonds change in time? The answer to this is yes, chemical bonds can change with time. When chemical reactions occur the bonds between the atoms change giving rise to new molecular species and the rate at which this occurs depends on the bond strength and the available energy. Hydrogen bonds are special cases of chemical bonds. With an intermediate bond strength between the covalent bond and Van der Waals interaction, hydrogen bonds are labile and dynamical [11].

Hydrogen bonding is responsible for the diversity of biological structures in nature. Crystals, liquids, and proteins are examples of hydrogen bonded systems in which the strength and the dynamics of this interaction differs substantially, see Figure 1.1. Seeking more information at the molecular level is crucial to understand these systems, and consequently to broaden the knowledge of the macroscopic phenomena arising from fast fluctuations of hydrogen bonded systems [12–20]. One of the first methods used to understand the properties of hydrogen bonds was infrared absorption spectroscopy [5]. The reason is that bonds, also hydrogen bonds, typically oscillate at defined frequencies in the infrared region of the electromagnetic spectrum.

However useful to understand structural properties, this method is not sensitive to dynamics arising from the fast fluctuations that characterize hydrogen bonded systems. To circumvent this limitation, and inspired by correlation Nuclear Magnetic Resonance (NMR) techniques [21, 22], two-dimensional infrared spectroscopy (2D IR) was developed [23]. This is correlation spectroscopy, which can provide dynamical information on very short time scales in the range from the femto ( $10^{-15}$ ) to pico ( $10^{-12}$ ) [23] second. Here, the absorption frequencies of the subsequently applied laser pulses are correlated giving rise to a 2D IR spectrum. Because of the fast speed of the measurements it is possible to retrieve information on the timescale of the chemical bond dynamics, hence, extracting fast dynamical details, for example allowing the real time observation of breaking and forming of hydrogen bonds. The peaks in the 2D IR spectrum contain dynamical information from the system, which can be extracted from the peak shapes and intensities. Information about the distance between the molecules and their relative orientations can be extracted from the spectral cross peaks, since they are a measure of the molecular couplings. Because of the crowded nature of the 2D IR spectra the interpretation is often very challenging. Thus, theoretical methods are crucial to provide deeper insight in a 2D IR spectrum and answer to questions that experimentalists alone cannot answer. Computational spectroscopy provides the theoretical tools to predict and interpret spectra [24–33].



**Figure 1.1:** Illustration of the electron density of a hydrogen bonded N-methylacetamide dimer, where the carbon atoms are represented in dark blue, the nitrogen in light blue, and the oxygens in red, and the hydrogens in white. The contours indicate the variation of the electron density varying from dark grey (less dense) to light grey (more dense).

In this thesis 2D IR spectroscopy is used to retrieve structural and dynamical properties of several hydrogen bonded systems, such as solvated molecules, and proteins. This is done by simulating relevant systems and comparing the results to experiment. Here, the aim is to extend our knowledge about the long timescale macroscopic phenomena that arise from hydrogen bonding fluctuations. In collaboration with experimentalist, our simulations provide insight in the experimental spectra, and provide a deeper understanding of the fast phenomena occurring in the systems. The theoretical approach is based on a combination of molecular dynamics simulations with response function calculations [27, 27–29, 32, 34–43]. The atomic coordinates generated by the molecular dynamics calculations are used to construct vibrational Hamiltonians, which are subsequently used in response function calculations to predict the spectra. The relevant parameters that determine the Hamiltonian, such as the site frequencies and the dipoles, are calculated using Density Functional Theory (DFT) based (electrostatic) maps, that relate these parameters to the electrostatic environment generated by the force field.

The following is an outline of this thesis on hydrogen bonding dynamics in condensed phase systems. In Chapter 2 a general introduction of hydrogen bonding in several systems is given. This chapter highlights the importance of hydrogen bonding in nature. The main goal is to introduce the concept of hydrogen bonding and to link it with the particular studied systems. Chapter 3 is dedicated to a general introduction to the field of computational spectroscopy. The main goal of this chapter is to describe the computational methods used to determine 2D IR spectra. The next chapter, Chapter 4, gives insight of the most proper electrostatic mapping and coupling models used to model the amide I mode spectra of protein systems. In Chapter 5, the delicate interplay between hydrogen bonding dynamics and exciton transfer in a protein-like liquid is discussed. In Chapter 6 a discussion regarding the temperature collapse and self-assembly of elastine like peptides is presented. Chapter 7 addresses the issues of dynamics of three bulk alcohols with different alkyl chains. Finally, in Chapter 8 three diluted alcohols and their vibrational dynamics are investigated, and along with this chapter an interesting perspective of the role of interactions in solvents and solutes is provided. At the end of this thesis the main findings are summarized.