

Chapter 1

Introduction

1.1 Hydrogen Bonds

Hydrogen bonds have been discovered in the beginning of the last century and have ever since drawn attention [1]-[7]. They are weaker than ionic or covalent bonds, but stronger than van der Waals interactions. Although they can easily be broken by thermal fluctuations, they govern the structure of a variety of systems. Many macromolecules, like DNA, proteins or cellulose, for instance, would not have stable conformations in the absence of this kind of interaction. Besides the conformation, they influence the dynamics of certain biological processes, for example, by assisting enzymes to bind to substrates. In other words, life would not be possible without them. Therefore, scientists have been trying for decades to unveil the reasons behind specific behavior of hydrogen bonded systems.

Hydrogen bonded molecules possess properties that differ from those of systems containing no such interactions. An illustrative example is liquid water, whose unexpectedly high heat of vaporization is due to the energy needed to break the numerous hydrogen bonds between the water molecules. Such *unusual* behavior had been observed long before the "hydrogen bond" obtained its name. Most of such observations date from the end of the 19th and the beginning of the 20th century. It was recognized that specific properties arise as a consequence of electrostatic interactions of a hydrogen atom H, which is covalently bound to an electronegative atom X (denoted as proton donor), and another electronegative atom Y (proton acceptor). An explanation has been proposed that in the observed cases a "weak bond" had been formed. However, it was Linus Pauling who first used the term *hydrogen bond* [1]:

"Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered as acting as a bond between them. This is called the 'hydrogen bond'."

In the early investigations mainly strong hydrogen bonds have been studied, with the donor and the acceptor being highly electronegative atoms, like fluorine, oxygen, or nitrogen. A few decades later, the definition was broadened, allowing less electronegative atoms, like carbon, silicon, phosphorus, to be involved in hydrogen bonding. On the other hand, only hydrogen and its isotopes can play the role of such a bridge between two atoms or two atomic groups. This is a consequence of hydrogen having solely one electron that can be attracted by the donor X, thus leaving the hydrogen nucleus to a great extent *free* to interact with the electron cloud (lone pairs or π electrons) belonging to the acceptor Y. Such strong deshielding of the nucleus has not been observed for any other element.

Substitution of hydrogen by deuterium leaves a negligible trace on the potential energy surface (PES), whose shape is governed by electrostatic interactions which are the same for H and D. However, other properties (vibrational spectra, dynamical processes, etc.) that depend on the masses of the constituents, are significantly affected by isotope replacement. This phenomenon, known as isotope effect, is pronounced to a greater or smaller extent depending on the strength of the hydrogen bond. Although the PES does not alter upon deuteration, the vibrational levels are shifted downwards, thereby inducing changes on the vibrational wave functions and modifying the internuclear distances. In this case we talk about the *geometric* isotope effect.

The most common classification of hydrogen bonds is performed with respect to their energy [4]: one distinguishes strong (15 - 40 kcal/mol), moderate (4 - 15 kcal/mol) and weak (1 - 4 kcal/mol) hydrogen bonds. **Strong** hydrogen bonds are usually referred to as *low-barrier hydrogen bonds*. In certain cases, the zero point energy might lie above the barrier. Strong hydrogen bonds are characterized by a small distance between the proton donor and the proton acceptor. Also, the donor/acceptor might have ionic character. If the donor is positively charged, it possesses deficiency in electron density, thereby attracts the hydrogen's electron, which leads to the deshielding of the proton. If the acceptor is negatively charged, that enhances Coulomb attraction with the proton. Either (or both) of those effects lead to a formation of a PES with a single minimum with the proton located close to the midpoint between the donor and the acceptor, so hydrogen motion is restricted to a small volume. Although hydrogen is in this case relatively rigid, it is responsible, for instance, for the catalytic activity of certain enzymes. **Moderate** bonds are the most common kind of hydrogen bonds. The donor and the acceptor atom are neutral species with the donor being more electronegative than the hydrogen, and the acceptor possessing a lone electron pair, that can interact with the proton. The PES is either characterized by a single minimum, or it exhibits a double minimum structure (which allows transfer of the hydrogen atom from the donor to

the acceptor atom, and vice versa). This flexibility of the bond enables molecules to take part in various chemical reactions, as well as processes in biological systems. Medium strong hydrogen bonds have been observed in all three phases. In solution, if the solvent is polar, additional hydrogen bonds can be formed between the solvent and the solute molecules. Also in crystals hydrogen bonds are recognized between neighboring molecules. **Weak** hydrogen bonds are characteristic for complexes in the gas phase, but have also been observed in crystal structures. The donor atom has a slightly higher electronegativity than the hydrogen atom, like C or Si, whereas the acceptor possesses π electrons. Also, forced weak bonds can be formed between pairs in the nucleotide crystals. For example, the planarity of the bases and the formation of medium strong N - H \cdots O and N - H \cdots N bonds forces the formation of C - H \cdots O and C - H \cdots N bonds.

1.2 IR Spectra of Hydrogen Bonded Systems

Experimental investigation of hydrogen bonds utilizing different methods is enabled by the fact that upon their formation various molecular properties change [4]. Prominent changes compared to the non-bonded systems are reflected in the structure of their infrared (IR) spectra (for an early review see [8]). In general, hydrogen bonded systems can be depicted as X-H \cdots Y. Hydrogen bonding represents a sort of perturbation, which introduces anharmonicity in the potential hypersurface, thus leading to different types of vibrational mode couplings. For instance, the force constant that governs the XH stretching vibration ν_{XH} becomes weaker, leading to a red shift of the band. Furthermore, it is to be expected that the XH stretching vibration couples to certain skeleton normal modes that alter the distance between the proton donor X and the proton acceptor Y (cf. Fig. 1.1). Those couplings allow appearance of combination transitions which might lie close to the ν_{XH} fundamental transition. In the condensed phase, the stretching band would thus not appear as a narrow line, but rather as a broad band. In addition, the so called *Fermi resonance* interaction, with combination and overtone transitions that include, e.g. the XH bending vibration, might lead to a peculiar substructure of the band. It took a few decades of joined experimental and theoretical investigation to prove that those features (red shift, broadening, substructure) are a consequence of anharmonic couplings of the stretching vibration to other molecular modes [6].

In the simplest case, only one skeleton mode is considered to be coupled to the fast XH stretching mode. It is usually chosen to be a low frequency mode that modifies the X-Y distance, ν_{HB} . Due to different time scales for the two vibrations, a second Born - Oppenheimer approximation (BOA) can be introduced, which separates those two types of motion. Compared to the standard BOA, the slow mode

takes the role of the "heavy nuclei", whereas the stretching vibration mimics the fast electrons. This means that the spectrum arising from such a model would correspond to a Frank - Condon like progression in the vibronic transitions of optical spectroscopy. Such situation is shown in Fig. 1.1.

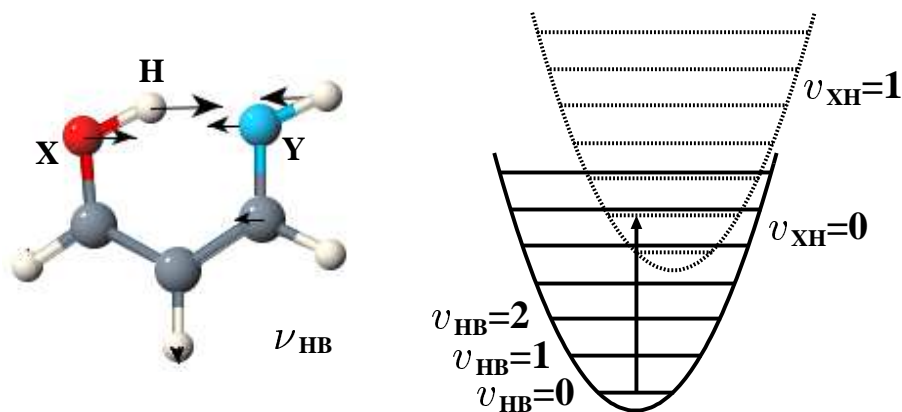


Figure 1.1: Left: 3-imino-propen-1-ol - low frequency mode that modifies the X-Y distance. Right: Energy levels in the spirit of the second Born - Oppenheimer approximation: the solid/dotted line corresponds to the ground/excited state of the XH stretching vibration. The vibrational levels describe excitation of the low frequency mode, like the one shown on the left side.

In the condensed phase, each of the series of lines is additionally broadened due to the interaction with the solvent [9]-[14], so in the high friction limit when the slow motion is damped all lines may be hidden underneath a single broad line. In the low friction limit, those lines are separated, leading to the appearance of a substructure.

This is a common explanation for characteristic features of IR spectra of hydrogen bonded molecules. Unfortunately, although the spectrum itself carries information on the presence of inter/intra molecular couplings, the only conclusion that can be obtained from the conventional IR spectroscopy is that the hydrogen bond does exist in the considered example and that certain couplings are responsible for the unusual behavior. The nature of those couplings, however, remains unknown, in particular in the condensed phase where any substructure might be hidden under a broad band. Nevertheless, since nuclear motions take place on a femtosecond time scale, they can be investigated by means of ultrafast spectroscopy [15]-[20]. A great merit for the development of femtochemistry goes to the group of Ahmed Zewail, who were the first to monitor nuclear motion during a chemical reaction, thereby getting a better insight into processes that occur while the chemical transformation takes place [21]. That is, the experimental realization of ultrashort laser pulses in the beginning of the last decade enabled to follow nuclear motion in real

time. This remarkable work was awarded a Nobel Prize in 1999. With the advances in laser technology, and in the understanding of molecular dynamics, there is a growing interest in laser control of chemical reactions [22] - [24].

A commonly used technique in femtochemistry is the pump - probe method

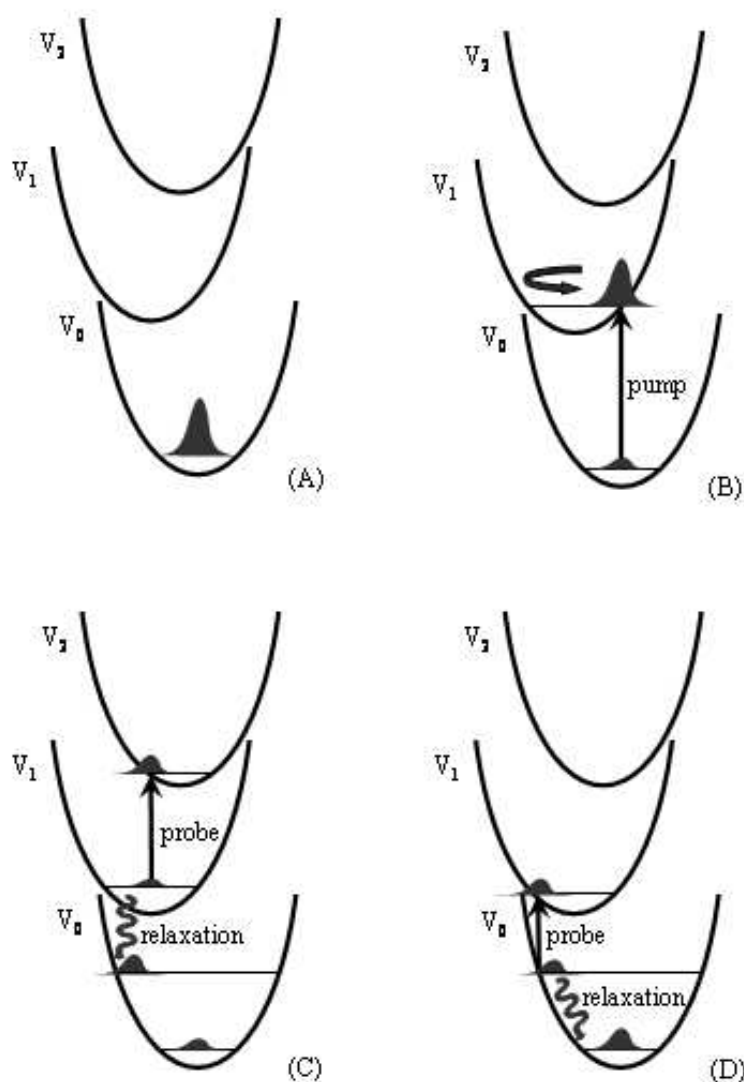


Figure 1.2: An illustration of a pump - probe method. (A) Potential energy surfaces of the ground (V_0) and the two lowest lying excited states, V_1 and V_2 . Initially the system is in the ground state. (B) The pump pulse excites the system to the first excited state, where the wave packet starts to move. (C) After a certain time delay, the state of the system is probed with a probe pulse that transfers part of the population to the higher excited state. At the same time, part of the wave packet relaxes to the ground state. (D) Another pulse "probes" the dynamics taking place in V_0 , thus examining the time scale of the relaxation processes.

[25], [26], shown in Fig. 1.2. Starting from the ground state V_0 , the system is promoted to an excited state V_1 , where a wave packet is constructed that represents superposition of eigenstates. The evolution of this wave packet is examined with the probe pulse, and by changing the delay between the pump and the probe pulse, the dynamics of the system can be followed. Thus, it is possible to investigate the relaxation phenomena related to the intra- and intermolecular energy redistribution - information unobtainable by conventional IR spectroscopy. It will be shown in the following chapters how the ultrafast phenomena can be used to study the origin of the shape of IR spectra.

1.3 Outline of the Work

In this work the dynamics of hydrogen bonded systems in the condensed and gas phase was investigated.

In Chapter 2, the theoretical methods of the quantum chemical and quantum dynamical calculations are presented. Special attention is paid to different ways of handling the anharmonicity of the potential energy surface, which is known to be responsible for the intramolecular vibrational redistribution (IVR) processes [27]-[29]. In this respect, the Anharmonic Force Field and the Cartesian Reaction Surface approach are detailed. Further, the Multi Configuration Time Dependent Hartree Method is introduced, which we used for propagations of the nuclear wave packets. For condensed phase calculations, the propagation of the density matrices is considered.

In Chapter 3 the dynamics of a hydrogen bonded system whose potential energy surface contains a single minimum, Phthalic acid monomethylester (PMME), is studied. In particular, the multidimensionality of the relaxation processes was investigated and the mechanism which includes both molecular and reservoir degrees of freedom was determined. Chapter 4 contains results for a double minimum system, Salicylaldimine (SA), with comparison of the properties of the protonated and the deuterated species. Those gas phase calculations reveal the strength of couplings between the reactive hydrogen atom and the skeleton modes, thereby providing a better understanding of the shape of linear IR spectra. Additionally, the possibility of a control of a hydrogen transfer reaction is discussed.

Finally, the work is summarized in Chapter 5.