Solvent Effects on Chemistry with Alcohols. An Ab Initio Study

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Chapter 4

Hydration/Dehydration Reaction between Ethanol and Ethene

We performed a DFT-based Molecular Dynamics simulation of the acid-catalyzed hydration of ethylene in aqueous solution under ambient conditions. As this reaction can be considered as a rare event we applied a constrained method. This method yields the free-energy barrier and can give clues how spontaneous events occur. Our simulation confirms the AdE3 mechanism at which two bonds are formed simultaneously causing a sudden change in its electronic structure and a flip from negative to positive constraint force. The specific structure of the hydrogen bonded network plays a crucial role in both the hydration reaction as in the reverse reaction. As it is not included in the imposed reaction coordinate it leads to hysteresis in a small window of the reaction coordinate.

4.1 Introduction

Hydration of ethene (also called ethylene) has been used in industry for large scale production of ethanol since several decades. In the industrial process the hydration of ethylene proceed in a gas-phase pressure recycling operation over solid phosphoric acid catalysts, manufactured by impregnating silica carriers [114, 115]. It may sound surprising that the reverse reaction, the dehydration of ethanol, is also used in industry for the synthesis.

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1This chapter is based on work in progress, to be published as a letter and as a full article: Titus S. van Erp, Evert Jan Meijer, "Ethene Hydration in Acid Solution. Revealing the Solvation Structure of Reacting Pathways" and Titus S. van Erp, Evert Jan Meijer, "Ab Initio Study:Hydration/Dehydration Reaction between Ethanol and Ethene"
for ethylene. Although this technology is now only of very limited importance because of the current availability of ethylene from more economical favorable petroleum based sources. However, the situation can be different for developing countries, that have scant petroleum resources, but do have substantial amounts of fermentation ethanol available derived from agricultural waste products. For them, a vapor-phase dehydration of ethanol is often the most efficient and economical way to produce ethylene [116]. The presence of the acid is of great importance for both industrial processes. It allows for a different reaction mechanism, which lowers the activation energy and increases the reaction rates yielding an energetically and economically favorable conversion. Baliga and Whalley [117] have measured the hydration of ethylene in dilute aqueous perchloric acid in the range of 170-190 °C at 100 bars and estimated a barrier height of 33.3 ±1.0 kcal/mol. Perchloric and sulfuric acids are known to be better catalysts than phosphoric acid in terms of conversion. However, industry uses phosphoric acid instead as side reactions are more suppressed for this catalyst. Still, the basic mechanism is roughly same for all acids. The important catalytic group of the acid is the positively charged proton that can easily split off forming a hydronium ion H$_3$O$^+$ when solvated in water. Therefore, if one wants to study the general mechanism of the acid catalyzed hydration in a molecular simulation, it is sufficient, to a good approximation, to limit the presence of the acid by the hydronium only.

If the catalyst is absent, the reaction barrier is about twice as high. MP2 calculations show energy barriers of 57.7 kcal/mol for the hydration and 67.1 kcal/mol for the dehydration reaction [118]. Consequently, this reaction will only occur under extreme conditions. The non-catalyzed dehydration reaction is experimentally observed for an ethanol molecule that is strongly vibrational excited via a chemical activation [118, 119] or by a pulsed HF [120] or CO$_2$ laser [121]. Theoretical calculations of rate constants were performed in the high temperature regime (700 K- 2500 K) [122] and for the laser induced decomposition of ethanol [123]. These measurements and calculations show that, for these conditions, the dehydration process yielding ethylene and water is the most favorable unimolecular decomposition reaction of ethanol.

The presence of an acid changes the reactive pathway and enhances the rate. If, in addition, the reaction evolves in a solvent, the reaction mechanism can be very complex as solvent molecules may participate in the reaction process. However, also the gas-phase association reaction between H$_3$O$^+$ and ethylene, and its reverse, the gas-phase dissociation of proto-
nated ethanol, have attracted scientists interest. The gas-phase association reaction is, for example, of importance for astronomical physics. It is believed that this process is responsible for the presence of ethanol observed in interstellar clouds [124]. The precise mechanism of this association reaction is still matter of scientific debates. There is evidence that the gas-phase formation of protonated ethanol $\text{C}_2\text{CH}_5\text{OH}_2^+$ has a $\pi$-complex $\text{C}_2\text{H}_4\cdot\text{H}_3\text{O}^+$ as an intermediate. In this complex the proton of the hydronium is bonded to the $\pi$-electrons of the double bond of the ethylene. For a single proton, computational studies to proton affinities have shown that the bridged $\pi$-bonded structure is more stable than the open ethylene cation [125–128]. Likewise, for the hydronium-ethylene complex, experimental [129–133] and theoretical [128, 132, 134] studies have shown the stability of the $\pi$-bonded ethylene-hydronium ion molecular associate $\text{C}_2\text{H}_4\cdot\text{H}_3\text{O}^+$. Therefore, it is believed that the mechanism for the gas-phase reaction between ethylene and the hydronium ion implies an indirect carbon protonation. First, the proton of the hydronium will approach the middle of the ethylene forming a bond to the $\pi$-electrons of the double bond. In a second stage, this proton will move to a carbon site and the $\text{H}_2\text{O}$ group to the other site forming the open structure of the protonated ethanol.

In general, one has to be cautious to make hard conclusions on the reaction mechanism in a solution based on the knowledge of the gas-phase results. An early experimental study to the acid catalyzed hydration of alkenes suggested that this $\pi$-complex also existed as an intermediate in the condensed phase [135]. Indeed, also for other alkenes than ethylene, the bridged structure seems to be more stable than the open cation structure [136, 137]. However, when solvation is taken into account energetics can change considerably. Jorgensen and Munroe have shown that the open ethylene cation is getting more and more favored to the bridged structure upon increasing solvation in HCl clusters [127]. Moreover, measurements of ethylene hydration in concentrated sulfuric acid advocate the proton attachment to the alkene directly through the formation of a carbocation [138]. Therefore, the general opinion is nowadays that for the hydration of olefins in the condensed phase the formation of an intermediate $\pi$-complex is not necessary.

Reactions in liquid water are of special interest as the role of the hydrogen bonded network of liquid water in chemical processes is presently subject of many discussions. In a broader perspective, this reaction can be related to other reactions in solvents in which proton transfer plays an important role. In this context we can refer to many other Car-Parrinello stud-
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ies (see e.g. [28,139–142]). Of great importance is also the pioneering work of Hynes and co-workers (see e.g. Ref. [143–148]) in which they deal with the solvent influence in proton transfer reactions by using a reaction coordinate that incorporates the degrees of freedom of the solution. More specifically related to this work is the ab initio study of Mohr et al [55], in which they showed that the hydrogen bonded network around an ethylene-cation radical can stimulate or prevent the hydration reaction depending on its precise structure. Recently, we showed that ethylene, usually considered as a hydrophobic molecule, can be induced to instantaneous dipole moments of $\approx 1$. D due to the polarization by the surrounding water molecules [149]. This points out that the presence of the solvent introduces many new effects that can significantly alter the reaction mechanism in comparison with the gas-phase reaction.

Molecular simulation provides an approach to study the microscopic behavior of liquids complementary to experimental studies. Standard molecular simulation techniques are based on empirical force fields that are designed to reproduce a selection of experimental data. Obviously, molecular simulations based on these potentials do not provide a picture completely independent from experiment. Moreover, the reliability of the results at conditions that are significantly different from those where the potential was designed for, may be questionable. Density functional theory (DFT) based molecular dynamics (MD) simulation, such as the Car-Parrinello molecular dynamics method [2], where the interactions are calculated by accurate electronic structure calculations, provides a route to overcome these limitations. Important advantages of DFT-MD over force-field MD are that it intrinsically incorporates polarization, that it accounts for the intra-molecular motion and therefore allows for a direct comparison with spectroscopy of intra-molecular vibrations, and that it yields detailed information on the electronic properties, such as the energy levels of electronic states and the charge distribution. The most important advantage is that DFT-MD, in contrary to force-field MD, is capable of studying chemical reactions. The making and breaking of chemical bonds are accompanied with huge changes in the electronic density. The forces in intermediate stages, during the chemical event, cannot be known a-priori, which makes the design of accurate force fields for these situations an almost impossible task.

We studied this reaction in both directions under ambient conditions in the presence of an aqueous solution. We limited the catalytic contribution to the addition of a single H$_3$O$^+$ to the solution. The accuracy of the used ab initio method for our system is supported by earlier work, such as the studies
of liquid water [14,90,91] and aqueous solvation [92–94,149]. This chapter is organized as follows: First we will discuss the computational method in section 4.2. In section 4.3 we will show the specific stages of the reaction when the system is forced over the barrier and estimate the free-energy barrier in section 4.4. In section 4.5 we will look in more detail to structural changes as function of our chosen reaction coordinate and as function of time when the reaction coordinate is fixed. Then in section 4.6 we will apply the Wannier analysis to obtain more insight in the electronic changes in the system. In section 4.7 we will look at the specific hydrogen bonded network structure to determine the topology conditions under which the reaction can take place. The conclusions are summarized finally in section 4.8.

### 4.2 Computational Methods

We performed MD simulations using the CPMD package [35]. This program combines MD motion of the ions with electronic structure calculations using the Kohn-Sham [9] formulation of Density Functional Theory (DFT) [8] in an efficient way using the Car-Parrinello algorithm [2]. This algorithm treats the basis set coefficients of the Kohn-Sham orbitals as dynamical variables and avoids in this way the expensive self-consistent field calculation, that have to be solved iteratively each time step for ordinary Born-Oppenheimer dynamics. Although the electronic wave function is never in its ground state during the simulation, it stays sufficient close so that the calculated forces on the ions are close to the true forces and deviations are not systematic and cancel out [21]. For the exchange correlation energy we chose the BLYP functional that includes Becke’s [11] gradient correction for the exchange energy of the uniform electron gas and the correlation functional of Lee, Yang and Parr [12]. This functional has proven to give a good description of liquid water [13,14], for proton transfer [28,139,141,142], for the aqueous solvation of alcohols [93,149], and the aqueous solvation of ethylene [149]. CPMD uses a plane wave basis set, matching the periodicity of the periodic box with waves up to a kinetic energy of 70 Ry. An uniformly distributed negative background charge was added to compensate the positive charge of the proton. Pseudopotentials were used to limit the number of electronic states to the valence electrons. Interaction with the core electrons was described by semi-local norm-conserving Martins-Troullier pseudopotentials [20]. Cut-off radii for H, O and C atoms were chosen to be 0.50 a.u. , 1.11 and 1.23 a.u. respectively for both l=s and l=p terms. The simulations were performed in a periodic box of length 10.19 Å , that matches to the experimental density
of the ethanol solution under ambient conditions. Starting from the ethylene side of the reaction, the box contained 31 water molecules, one H$_3$O$^+$ for the acidity, and one ethylene molecule. Temperature was controlled by a Nosé-Hoover [42–44] thermostat and fixed at 300 K. The fictitious mass associated with the plane-wave coefficients is chosen at 900 a.u., allowing a time step for the MD ions motion of 0.145 fs.

$Ab Initio$ MD simulations are computationally demanding and typical simulation times are consequently limited to $\approx$ 10 pico seconds. In view of the large reaction barrier, the chance that within this short period a spontaneous reaction occurs is negligible. To enforce the reaction we use the constrained dynamics method combined with thermodynamic integration (see e.g. [23]). This method requires a definition of a reaction coordinate that connects reactant and product side. With the reaction coordinate fixed by constrained MD, the time average constraint force can be measured. Proper integration of this mean force over the reaction coordinate yields the reversible work or the difference in free-energy. By making a series of simulations, each with a different value of reaction coordinate in the intermediate range between reactant and product state, one can numerically approximate this integration and obtain the free-energy profile and thus the activation and reaction energy. Recently the corrections to the mean force to obtain the exact free-energy have been outlined [24, 25]. However it has been shown that this kind of corrections to similar systems are of minor importance [28, 150]. We have chosen a reaction coordinate $Q$ similar to [28], that controls the transfer of the proton to the ethylene carbon. This reaction coordinate $Q$ is defined as the difference between two distances: $Q = |O-H| - |H-C|$ where O and H are the oxygen and hydrogen of the hydronium ion and the C is one of the carbons from the ethylene molecule. This constraint controls the proton transfer from the hydronium ion to the ethylene molecule. This is the reaction step with the highest energy barrier and is the only part of the reaction, that we force by our constraint. A negative value of $Q$ implies that the proton H is close to the oxygen O forming a hydronium ion H$_3$O$^+$, while positive value means that the proton is closer to the carbon C. Note that this definition of $Q$ allows a lot of flexibility. When $Q$ is fixed, the $|O-H|$ and $|H-C|$ distances can still fluctuate in time. This allows the reaction to evolve in a more free way, than if we would have chosen for a more simple reaction coordinate such as the $|C-H|$ distance. In total we performed 21 simulations in which $Q$ was fixed at different values in the range $[-1.59 \text{ Å} : 1.59 \text{ Å}]$. The values close to the transition state around $Q = 0 \text{ Å}$ were performed over simulation times of approximately 10 ps. In this range hysteresis oc-
curs. Therefore, performed in this range simulation series with increasing and decreasing $Q$, in the following indicated by "(hydration)" and "(dehydration)". For the values $|Q| > .212 \text{ Å}$ shorter simulation times of 5 ps were performed. In this range there is no hysteresis. All simulation data were sampled after 0.7 ps of equilibration time.

4.3 Mechanism

We started with a simulation without any constraint at the ethylene side. The extra proton in solution can be freely transferred along hydrogen bonds between water molecules. We waited until a hydronium was formed close to the ethylene and then we applied the constraint. Starting point of the series of simulations was a constraint value of $Q = -1.06 \text{ Å}$ at which a simulation of 5 ps was performed. In this simulation the selected proton is on average $2.07 \text{ Å}$ away from the carbon atom and $1.01 \text{ Å}$ from the oxygen. In panel A) of Fig. 4.1 we see a particular snapshot of this simulation. One of the other non-constrained hydrogens of the hydronium ion has moved towards one of the neighboring water molecules. We observed that the proton transfers of these hydrogens for this $Q$ value was limited to the first neighboring water molecules and that these hydrogens always returned to the constrained-oxygen. Thus, the positively charged proton was not lost in the solution but remained close to the ethylene. Therefore, extra constraints on the hydronium ion were not needed.

The $Q = -1.06 \text{ Å}$ simulation was followed by a series of subsequent simulations where we moved the proton towards the ethene-carbon. Panel B) of Fig. 4.1 shows a snapshot of the simulation $Q = 0.0 \text{ Å}$ (hydration), where the proton H is forced to stay exactly in between the oxygen and the carbon. Proton transfers of the other non-constrained hydrogens to neighboring water molecules were no longer observed, indicating that the molecular bonds between the oxygen and these hydrogens are stabilized. The $|C-H|$ distance is strongly fluctuating in the range $[1.24\text{Å} : 1.58\text{Å}]$. Bonds between atoms in this figure are drawn according to distance dependent bond definitions, that assigns a CH bond when the interatomic distance is less than 1.31 Å and a OH bond when it is less than 1.27 Å. The simulation movie for this constraint value shows a constant appearance and disappearance of the two bonds. In section 4.6 we try the give a more elucidated definition of a bond not only dependent on the distance.

Panel C) of Fig. 4.1 is a snapshot for the constraint value of $Q = +0.106 \text{ Å}$ (hydration). The average $|C-H|$ distance is decreased compared to pre-
Figure 4.1: Four snapshots from four different simulations, each with a different constraint value for $Q$. The important atoms and bonds are visualized by ball stick representation, the others by sticks. Dark grey indicate oxygen, white hydrogen and middle grey carbon atoms. The white dashed lines indicate the hydrogen bonds between the waters and there is a dashed line that connects the three atoms that determine $Q$. The constraint values are, A): $Q = -1.06 \text{ Å}$, B): $Q = 0.0 \text{ Å}$ (hydration), C): $Q = 0.106 \text{ Å}$ (hydration) and D): $Q = 1.06 \text{ Å}$. Each picture shows one typical time shot of four simulations.

vious $Q = 0.0\text{ Å}$ (hydration) simulation. However, in this typical snapshot the instantaneous distance is a bit higher than in panel B). The interatomic distances are beyond the distance of what one would normally assign for a bond. Therefore, the constrained-proton looks isolated not forming a bond with either the carbon or the oxygen atom. In section 4.6 we show however that this picture is misleading. Contrary to the distance dependent
bond definitions, but based on electronic density, one does can speak of a stable CH bond in panel C) and not in panel B). At the other side of the ethylene, one of the waters out of the solution has formed a bond to the other carbon. This reaction step happens spontaneously when the reaction coordinate $Q$ is fixed at this value.

The last panel D): $Q = +1.06 \text{ Å}$, shows that the proton has moved closer to the carbon almost at the ideal CH bond length of 1.10 Å. At the other carbon the CO bond has remained stable for all $Q > 0.106 \text{ Å}$ and protonated ethanol has been formed. Subsequently, the protonated ethanol loses one proton at the oxygen site. Apparently the barrier for deprotonation of the protonated ethanol is small or absent. This is consistent with a recent study of hydrated methanol clusters [151] that show that for the largest cluster considered (H$^+$CH3OH(H2O)$_6$) energy differences between configurations with H$^+$ attached to either methanol, water, or the H$^+$ in between methanol and water are very small. The issue of deprotonation of aqueous protonated alcohols is presently under investigation [152].

### 4.4 Energetics

The time-averaged constraint force is plotted in Fig. 4.2. We see that, for large negative and positive $Q$ values, the force is approaching zero. For the transition region $Q \approx 0 \text{ Å}$ we detect sudden jumps in the mean force. From left to right the force chances from negative to positive sign. This is directly related to the formation of the CO bond at the other carbon. When we start from a configuration where this CO bond is established and decrease the reaction coordinate again, this CO bond is not directly broken. The solvation shell has to rearrange before the reaction will occur backwards, which gives rise to hysteresis. Similar effects were found in the $S_N2$ reaction between CH$_3$Cl and Cl$^-$ [150] and in the acid catalyzed addition of water to formaldehyde [28] in aqueous solution.

For the reaction coordinate $Q = 0.053 \text{ Å}$ we found two almost stable configurations, $Q = 0.053 \text{ Å}$ (hydration) and $Q = 0.053 \text{ Å}$ (dehydration). The $Q = 0.053 \text{ Å}$ (hydration) configuration was stable during the complete 10 ps simulation. For the $Q = 0.053 \text{ Å}$ (dehydration) configuration the CO bond stayed intact for about 8 ps when suddenly this bond was broken and the constraint force swapped from a positive to negative value. Also in the $Q = 0.106 \text{ Å}$ (hydration) and $Q = 0 \text{ Å}$ (dehydration) simulations, a sudden reactive event was observed after 2 and 3 ps respectively.

The mean force was integrated by taking the stable point values and
Figure 4.2: Top: the average mean force as function of reaction coordinate $Q$. Values for $|Q| > .2$ Å were obtained after averaging over a MD run of at least 5 ps, for $|Q| < .2$ Å more than 10 ps simulation runs were applied. Each run started with .7 ps of equilibration for which no data was collected. Both direction (hydration) and (dehydration) are indicated by solid and dashed lines respectively. There is hysteresis in a small window with a strong change in the mean force. The arrows indicate that during the simulation run a flip in the constraint force was observed in the direction of the arrow. Bottom: The integrated curve yielding a free-energy barrier of 23.3 kcal/mol and a reaction energy of 5.3 kcal/mol.

the weighted average for the two $Q = 0.053$ Å cases. The obtained free-energy barrier is 23.3 kcal/mol, while the reaction energy is 5.3 kcal/mol as
4.4 Energetics

is shown in the lower panel of Fig. 4.2. The barrier is 10 kcal/mol lower than the experimental value of Baliga and Whalley [117], who found a reaction barrier of 33.3 ±1.0 kcal/mol. However, static BLYP calculations with perchloric acid in the gas-phase shows a similar barrier of 24.7 kcal/mol [153]. It is a known feature that DFT tends to underestimate barrier heights to some extend (see for example Ref. [150]). The comparison between our result and the gas-phase BLYP calculation of Ref. [153] is complicated by two factors. First of all the mechanism is different, where in the gas-phase reaction the hydrating water molecule also provides the proton, whereas in the our solution-calculation the proton providing water and the hydrating water are different molecules approaching the ethylene molecule from opposite side. Secondly, it should be noted the approximate reaction coordinates we have chosen gives rise to a underestimate of the true reaction barrier. To arrive at a better insight of the effect of the solvent we performed some calculations of protonated hydrated ethylene configurations mimicking the mechanism observed in solution. Preliminary calculations show that for a cluster with a single H$_3$O$^+$ providing the proton and a single hydrating water molecule at the opposite side of the ethylene molecule the barrier is absent. A small barrier of ≈ 4 kcal/mol appears of both the H$_3$O$^+$ as the hydrated water molecule are solvated by two water molecules. This suggests that the solvation effects play a significant role increasing the barrier in the order of 20 kcal/mol. Note that these processes are highly unlikely in the gas-phase as they require simultaneous collisions between three or more molecules.

Obviously, the catalytic effect is significant as a decrease of 30 kcal/mol implies an increase to the reaction rate in orders of magnitude. We can make an additional comparison to acid catalyzed hydrations of other alkenes. An early measurement of Lucas and Liu [154] showed a reaction barrier of 18.9 kcal/mol for the acid-catalyzed hydration of trimethylethylene. This lower activation energy is consistent with the view that larger molecules are better able to delocalize the charge allowing for a more stable transition state [155].

The calculated reaction energy in solution of 5.3 kcal/mol is lower that the MP2 value of 9.4 kcal/mol [118,119] and the BLYP-CPMD value of 9.09 kcal/mol [149]. However, the latter values are just energy differences and do not take the change in entropy into account. The entropy is higher at the ethylene side, as here is one extra water molecule in solution that can freely move. This lowers the free-energy at that side and thus decreases the free-energy difference between reactant and product side, or equivalently the reaction energy.
4.5 Structural Properties

In Fig. 4.3 we showed two relevant time averaged interatomic distances as function of the reaction coordinate. The distance $|\text{CH}|$ is the distance between the carbon and the hydrogen, that is partly controlled by the constraint $Q$. The other distance $|\text{CO}|$ is the distance between the other carbon and the closest water-oxygen. Note that this is not always the same oxygen as water molecules move to and away from the ethylene molecule during the simulation. Surprisingly, in the reactive region around $Q = 0$ Å there is no noticeable decrease in the $|\text{CH}|$ distance, whereas the mean constraint force shows a sudden change from a negative to a positive value. The depicted $|\text{CO}|$ distance instead shows a clear and sudden decrease as function of $Q$ in this region. The hysteresis effect is also clearly noticeable here, while for the $|\text{CH}|$ curve the (hydration) and (dehydration) values almost completely coincide. Furthermore, when looking to the $|\text{CH}|$ curve, we see that it is gradually decreasing and it is difficult to pinpoint where a real molecular bond is formed. Finally, for $Q > .5$ Å the distance seems to be converged to its normal bond length of 1.10 Å.

![Figure 4.3: Time averaged distances as function of the constrained value $Q$. Top: $|\text{CH}|$ is the distance between the constrained hydrogen atom and carbon atom. Bottom: $|\text{CO}|$ is the distance between the other carbon and the closest oxygen atom from the liquid water. Note that this oxygen by this definition does not necessarily belong to the same water molecule. The (hydration) and (dehydration) indicate that the simulation started from the ethylene or ethanol side respectively](image)

In Fig. 4.4 we show the time evolution of these two distances for two...
specific ‘reactive’ simulations: $Q = 0.053 \text{ Å}$ (dehydration) and $Q = 0.106 \text{ Å}$ (hydration). Clearly the $|\text{CO}|$ distance and the constraint force are strongly correlated, with the two graphs almost as if they were mirror reflections. The $|\text{CH}|$ distance shows almost no correlation with the constraint force. For the $Q = 0.106 \text{ Å}$ (hydration) we can detect only a bit more fluctuative behavior in the reactive time domain. As the constraint force acts on these atoms and a fixed reaction coordinate $Q$ allows changes in the $|\text{CH}|$ distance, one would expect a stronger effect. Fig. 4.4 shows, however, that the constraint force changes sign, indicating that the proton is now attracted to the carbon instead of to the water oxygen, without influencing the interatomic $|\text{CH}|$ distance.

![Figure 4.4: constraining force, distances $|\text{CO}|$ and $|\text{CH}|$ as function of time for two 'reactive' simulations: $Q = 0.053 \text{ Å}$ (hydration) and $Q = 0.106 \text{ Å}$ (dehydration). Average values of each these two simulation runs are depicted in Fig. 4.2 and Fig. 4.3 as one point each.](image)

### 4.6 Electronic Structure

From the previous we can conclude that, although the constraint force suddenly changes, the structural changes occur at the other side of the molecule.
Somehow the structural changes at that side of the molecule must change the affinity of this proton to form a bond with the carbon or with the oxygen. A change in the electronic structure must be the cause of this phenomenon. To quantify the electronic density distribution we used the method of maximally localized Wannier functions whose centers (WFC) can be assigned with a chemical meaning such as being associated with an electron bonding or lone-pair [111] and can also be used to calculate individual dipole moments of molecules in solution [106, 112, 113, 149]. The dipole moment of a single molecule can then be approximated as if it consists of point charges located at the atom positions and on the WFC positions, at atom positions a positive charge equal to its atom number minus its core electrons and at the WFCs a negative charge of -2 e. The total number of WFCs is the total number of valence electrons divided by two and its positions can give a clear insight in the electronic changes of the system during a reaction. From our series of simulations we took a few snapshots at important points just before and after a reaction. On these configurations we applied the Wannier function analysis to detect the electronic changes. We did not make enough calculations to obtain accurate statistical averages, but our aim was to see on a more qualitative level how the electronic structure is changing in the reactive process. Ethylene has in total six Wannier orbitals, four at the CH bonds and two, forming the double bond in the middle of the carbons just below and above the plane of the ethylene molecule. The water molecules have in total four WFCs tetrahedrally oriented around the oxygen, two of them forming the OH bonds and the other two indicating the lone pairs. The situation for hydronium is more or less the same, but then three form an OH bond and only one WFC is left at the oxygen site. Fig. 4.5 gives in a cartoon illustration of the observed structural and electronic changes of the reaction.

Panel 1) is the typical situation for $Q$ around -0.5 Å. The hydronium OH bond is directed towards the middle of the CC-bond. The WFC below the ethylene plane is attracted by the positive charge of the hydronium and is shifted slightly towards this proton. This cause an increase of the angle $\alpha_1$ from 27° to 35° and induces a dipole moment orthogonal to the plane of the ethylene molecule with a strength of approximately 1.9 D. This is a significant dipole moment, approximately equal to a water molecule in the gas-phase [112, 113]. The interaction between the hydronium OH bond and the WFC of the double CC bond can be considered as a kind of hydrogen bond. In Ref. [149] we showed that even in a neutral aqueous solution this effect is also significant and can induce instantaneous dipole moments of
1.0 D to a solvated ethylene molecule. It is not surprising that the effect of the hydronium ion is even stronger. The upper Wannier orbital has also moved a bit downwards to the middle of the CC bond, but this shift is much smaller.

Step 2) is the situation for $Q$ around zero. The constrained proton is in the middle of the carbon and the oxygen. The induced dipole moment is no longer exactly orthogonal as the lower WFC has moved away from the middle and is now closer to the left carbon. $\alpha_1$ has become approximately 50° and $\alpha_2$ is approximately 120°. Clearly, the proton attack is directing to the carbon site and is not forming a bridged structure. This observation is consistent with the experiments of Nowlan and Tidwell [138] and the calculations of Jorgensen and Munroe [127], that indicate that the protonation in
a solution is approaching directly to the carbon site and that the formation of an intermediate π-bonded complex is not necessary.

Step 3) is a situation for \( Q = 0.106 \) Å (hydration). \( \alpha_1 \) has increased till 50-80°, while \( \alpha_2 \) is still around 120-130°. The lower WFC is further away from the right carbon, which make this side more positively charged. It is a general feature of protonation, that the charge donation to the proton comes primarily from the terminal atom rather than the atom bonded to the proton [126]. Incidentally, water molecules at the other side approach the other carbon at distances of 2.6 Å, but usually are rejected back unless this coincides with a ideal solvation structure.

This brings us to step 4), the same \( Q \) value, but later in time. The incoming water molecule and the solvation structure around it have found a proper configuration for a nucleophilic attack. The CO distance rapidly decreases and forms a bond. Fig. 4.4 shows that there is a chance that directly thereafter this water is rejected back to the solution. The specific water configuration has decreased the reaction barrier, but this is also true for the backward reaction. This can induce a sequence of hydration and dehydration reactions, but at some moment the situation stabilizes and the water gets definitely attached to the carbon. The \(|\text{CH}|\) distance in this reaction process does not chance that much, but the lower WFC flips over 30-40° more in line to the CH bond, yielding \( \alpha_1 \approx 100° \) and \( \alpha_2 \approx 170° \). Whereas first, this WFC was playing part in both the bonding between the two carbons and between hydrogen and the carbon, now its function is only the CH bond. The increase of \( \alpha_1 \) over more than 90° indicates that this WFC does no longer take part in the CC bond. The constraint force on the proton H is first repulsive with respect to the carbon, while after the transformation it becomes suddenly attractive. The fixed constraint \( Q \) prevents however that the CH bond will fully relax to its rest value. The carbon, the WFC, and the proton are almost in line according to \( \alpha_2 \approx 170° \). This gives a clear indication that the CH bond is formed. Moreover, the fact that now only one WFC is positioned in the middle of the two carbons followed by the out-of-plane bending of the ethylene-hydrogens shows clearly the change from sp2 to sp3 hybridizing of the CC bond.

The Wannier analysis shows that both molecular bonds, the CH and the CO bond, are formed simultaneously. This indicates that the process occurs following an AdE3-type mechanism. Conversely, the dehydration reaction follows the E2 mechanism, being the inverse of the AdE3. The alternative AdE2 hydration and E1 dehydration mechanisms imply a stable ethylene cation as intermediate. Although, several undergraduate text books use
the E1 mechanism for the description of the acid catalyzed dehydration of ethanol (and, similarly, an AdE2 mechanism for the acid catalyzed hydration of ethylene), the current opinion is that a concerted E2-type mechanism more probably governs the hydration of primary alcohols [5, 6]. Consistent with this view are the experiments of Baliga and Whalley that indicate a transition state for the hydration of ethylene with at least one firmly bound water molecule [117].

4.7 Hydrogen Bonds

In this section we will discuss the role of the hydrogen bonded network of the liquid water for this reaction. The constraint values for which we observed a spontaneous reaction are: +0.106 Å (hydration) and 0.0 Å (dehydration), +0.05 Å (dehydration). The spontaneous reaction step that is not controlled by the constraint is the formation or breaking of the CO bond. From our simulation with \( Q = +0.05 \) Å (dehydration) we saw that the protonated ethanol and thus the CO bond was stable for about 8 ps, when suddenly the \( \text{OH}_2 \) group was split off. We estimate a distance between the carbon and the oxygen of 1.8 Å that we call a critical dehydration distance. Incidentally, due to fluctuation in the molecule the CO distance stretches beyond this critical distance as shown by Fig. 4.4. As the vibrational energy itself is not large enough to break this bond, it must be a specific hydrogen bonded structure that, at a certain moment, pushes the reaction just over the barrier. This happens only when such an extreme fluctuation beyond 1.8 Å coincides with a specific solvation structure. To examine this we compared a few cases where this critical situation was reached and looked why in one case the reaction was successful and in the other not. The top panels of Fig. 4.6 show two typical cases that are very similar in structure from the same \( Q = 0.053 \) Å (dehydration) simulation, but at different times. Only the important molecules and WFCs are visualized. The left situation at \( t = 3.03 \) ps shows an unsuccessful and the right one at \( t = 8.14 \) ps shows a successful dehydration configuration. The |CO| distances are 1.805 Å and 1.786 Å respectively and the |CH| distances are 1.32 and 1.35 Å. The two situations are almost identical except that in the second case the protonated ethanol forms three hydrogen bonds, donating two and accepting one, while in the first configuration there are only two donating hydrogen bonds. We checked this for the whole simulation run up to the moment of reaction, and it was found that \( \text{OH}_2 \) group of the protonated ethanol was constantly bounded by two hydrogen bonds, in which the \( \text{OH}_2 \) group acted as proton donator.
The times that it also accepted a proton via a hydrogen bond were rare and there was no overlap with the fluctuations larger than 1.8 Å, until just before the reaction point at $t = 8.14$ ps.

![Figure 4.6: Four structures obtained from two simulations. Dark grey indicate the oxygens, white the hydrogen, middle gray the carbons and light grey the WFCs. The dashed lines indicate hydrogen bonds and other weak attracting forces between WFCs and atoms. Top left panel: $Q = 0.0529$ Å (dehydration) at 3.03 ps, top right panel: $Q = 0.0529$ Å (dehydration) at 8.14 ps. Bottom left panel: $Q = 0.106$ Å (hydration) at 1.52 ps, Bottom right panel: $Q = 0.106$ Å (hydration) at 1.97 ps.](image)

For the hydration reaction case $Q = 0.106$ Å (hydration) we estimated the critical hydration distance for the incoming water to be 2.6 Å and postulated that the reaction can only be successful when the water approaches from the other side of the ethylene plane with respect to the hydronium ion. Again we looked closely at similar configurations. At the bottom panels we see two snapshots of the $Q = 0.106$ Å (hydration) simulation, one at 1.52 ps and the other at 1.97 ps. The $|CO|$ distances are 2.63 Å and 2.64 Å respectively and the $|CH|$ distances are 1.39 and 1.37 Å. Although, in both situations the attacking water molecule is three times hydrogen bonded, only the last one was successful. We must conclude that the possibility of a reaction is not simply depending on the number of hydrogen bonds, but depends
in a more subtle way on the precise hydrogen bonded structure. Further examination of the two panels gives a clue what could be the crucial difference between the two configurations. If we relate the axis between the carbon and the middle water molecule with the hydrogen bonds around this water, we can detect a kind of umbrella structure. We think that the right panel is more favorable as it is much more similar to a tetrahedral structure. In this case the three outer water molecules position the middle one in an ideal orientation with its free WFC in a perfect line between its oxygen and the (positively charged) carbon of the ethylene. The other situation deviates significantly from the ideal tetrahedral configuration. To restore a more tetrahedral configuration the central water molecule has to move upwards, removing it from the ethylene molecule and thus leading to a non reactive event. More quantitative, the COO angles in the left panel are from left to right: 112.0°, 89.4° and 149.3° and in the right panel they are: 105.7°, 98.1° and 118.4°. The latter case is indeed much closer to the tetrahedral structure with angles of 109°.

4.8 Conclusions

We performed a DFT-based based Molecular Dynamics simulation of the acid-catalyzed hydration of ethylene in aqueous solution under ambient conditions. To overcome the reaction barrier, we used the constrained dynamics method in combination with thermodynamic integration to obtain the free-energy profile along a chosen reaction coordinate. We found a reaction barrier of 23.3 kcal/mol and a reaction energy of 5.3 kcal/mol. This is much lower than the experimental barrier of 33.3 ±1.0 kcal/mol [117]. However, the BLYP functional underestimates the reaction barrier to some extent and the approximate reaction coordinate gives probably an additional underestimation of the barrier. A DFT-BLYP calculation of the gas-phase reaction showed a similar barrier of 24.7 kcal/mol [153]. However, the comparison is somewhat misplaced as the mechanism for the reaction is different, where in the gas-phase reaction the hydrating water molecule also provides the proton, whereas in the our solution-calculation the proton providing water and the hydrating water are different molecules. Primarily calculations suggest that the latter mechanism in the gas-phase, involving the H₃O⁺·C₂H₄·H₂O complex, has no barrier at all. In that sense, one could say that the solvent effects increase the barrier by about 20 kcal/mol. Though, this process is not so likely in the gas-phase as it requires a simultaneous collision of three molecules.
The protonation of the ethylene is directly pointed towards the carbon site without the formation of a $\pi$-bonded bridged structure as an intermediate. Moreover, our simulations confirm the assumption that the reaction follows the AdE3 mechanism for which simultaneously two bonds are formed. The $|\text{CH}|$ distance is minimally changing after the reaction has been established, but the constraint force has a sudden change from repelling to attracting the proton towards the carbon. We studied this effect by the Wannier analysis of the electronic structure. The WFC participating in the double bond between the carbons has a sudden change and moves away from the ethylene center more in alignment with the CH axis. This indicates a change from sp2 to sp3 hybridization and the formation of a CH bond. The Wannier analysis gives in this way clear information on how and when molecular bonds are formed, which is not possible to achieve from the atomic positions only. Furthermore, we looked at the specific hydrogen bonded network that enables a reaction to occur when the reaction coordinate is fixed close to the top of the free-energy barrier. The increasing constraint value transfers the proton towards the carbon and polarizes the ethylene molecule, yielding a positively charged carbonium ion at the other side. This enables the spontaneous formation of a CO bond between that carbon and a water molecule from the solution. For the dehydration reaction of the protonated ethanol we found that when due to spontaneous fluctuations the CO bond is over stretched beyond 1.8 Å and simultaneous the OH$_2$ group of the protonated ethanol has more than two hydrogen bonds, the reaction is likely to occur. For the hydration reaction we found that the attacking water molecule should approach at a distance of 2.6 Å. Mostly, this water will be rejected back into the solution. However, when this water has three hydrogen bonds and the COO angles are close to the tetrahedral value of 109° the hydration can occur and protonated ethanol will be formed. This proves once more the solvation structure participates strongly in the mechanism and is, therefore, part of the true reaction coordinate [143–148]. This study shows that the occurrence of a reactive event depends on the solvation structure in a very subtle way. Our simulations suggest that the reaction is initiated by a number of effects, in which both rare fluctuations of the solute molecule as the occurrence of properly structured water groups play a crucial role.