

# Hydrolysis of Metal Ions from the Perspective of Proton Transport in Liquid Water

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The dynamics of proton transfer reactions still persists as an open question to both experimentalists and theoreticians. Theoretical studies on liquid water indicate that the molecular processes involved occur at timescales transparent to conventional detection. In contemporary models, the anomalous diffusion of a proton in liquid water appears to be closely tied to how hydrogen bonding patterns evolve, which suggests that proton dissociation proceed only if certain conditions are met: structural patterns and dynamics satisfied over a network of hydrogen bonded molecules. These have been verified through simulations of highly charged metal ions in aqueous solution in which quantum mechanical calculations are explicitly invoked to allow the occurrence of hydrolytic events. The results obtained thereof have given insight into the proper evaluation of proton transfer events and how they can be understood in the context of many body interactions.

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## INTRODUCTION

Over 200 years have passed since Theodor Christian Johann Dietrich von Grotthuss rationalized the anomalous mobility of protons in liquid water by what is now more commonly known as the “proton-hopping mechanism” or simply the “Grotthuss mechanism” (de Grotthuss, 1806). As opposed to the gradient-controlled diffusion of small ions in liquid water, the structural diffusion described in the Grotthuss model involves the sequential transfer of a proton along adjacent water molecules in a “bucketline” fashion (Marx, 2006). The subtleties of this theory, of course, necessitate

a significant degree of scrutiny on the motion of water molecules in the liquid state, as they may very well be perceived as the factors that limit proton migration from one water molecule to the next. For the best part of its inception, the concept had stayed in the realm of theory until the dawn of ultrafast detection methods (Weiner, 2009; Reid and Wynne, 2000), which enabled researchers to monitor processes occurring in the femtosecond timescale, thus allowing for finer inspection of very fast molecular motions consistent to different types of dynamic phenomena. However, these methods cannot directly elucidate the mechanisms characterizing proton transport but serve primarily to

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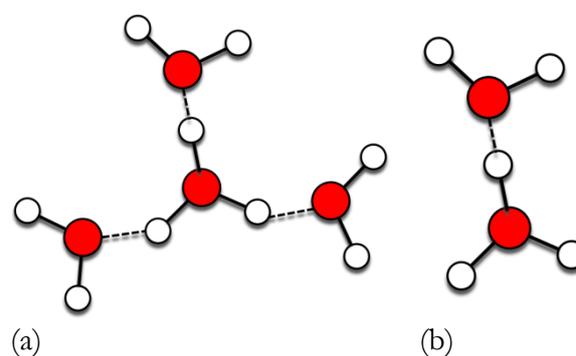
measure the presence of structural/dynamical markers proposed in the Grotthuss model. For example, the vibrational signatures of hydrate complexes of the excess proton have been studied using femtosecond pump-probe measurements in the Mid-IR range (Kim et al., 2002; Woutersen and Bakker, 2006; Roberts et al., 2009).

While the purpose of this paper is not to shed new light on the anomalous diffusion of a proton in liquid water, a special consideration of the properties of a solvated proton would nevertheless benefit the discussion of one related phenomena: hydrolysis of metal ions in aqueous solution. To this end, it becomes appropriate to discern the mechanism involved in the dissociation of a proton from a water molecule interacting with a highly charged metal ion in much the same way as with a hydrated proton transiting in the liquid phase of water. Unlike bulk measurements, the elucidation of processes evolving in the molecular level are highly sensitive to thermal fluctuation and thus offers a different level of complexity that forces investigations in this area to rely heavily on theory.

## STRUCTURAL DIFFUSION AND THE COMPLEXES OF WATER

From the Grotthuss theory, questions more particular to structural aspects of the proton-hopping process arose. At any point in time, a proton must interact with surrounding water molecules with a corresponding configuration that is pre-disposed to proton transfer. These structures identify to low energy configurations that may interconvert rapidly in solution. Eigen and his co-workers suggested that once a hydronium ion is formed it would be immediately be solvated by three water molecules to form a transient complex (Figure 1a) ( $\text{H}_9\text{O}_4^+$ ) (Wicke et al., 1954). On the other hand, Zundel and his collaborators proposed that, instead of the formation of a transiently solvated hydronium ion, an excess proton is shared between two water molecules (Figure 1b) ( $\text{H}_5\text{O}_2^+$ ) prior to an actual proton transfer (Zundel and Metzger, 1968). Though largely conceptual, the Eigen and Zundel complexes are perhaps the most widely accepted

structural indicators of the structural diffusion of a proton under the Grotthuss model, and much of the contemporary researches on water still focus on the elucidation of these complexes whether from experimental or theoretical methods.



**Figure 1.** Schematic representation of the (a) Eigen and (b) Zundel complex. Dashed lines indicate hydrogen bonding. In the case of the Zundel complex, the proton is shared nearly equally between the two oxygens.

Of course, one may be quick to observe from the Eigen and Zundel complexes the special role of hydrogen bonding in proton transport. Indeed, it is easy to imagine an assembly of hydrogen bonded water molecules as the bucketline in which the proton-hopping process can occur. For the structural diffusion of a proton to happen very quickly, adjacent water molecules must be oriented against each other in such a way as to provide the lowest barriers to proton transfer. The relative stabilities of the different coordination environments available to a proton determine the pre-disposition towards a particular hydrogen-bonded configuration as the well as the rapid transformations from one to the other along the hopping process.

The wealth of studies done to capture the collective dynamics of water molecules in the liquid state attest to the importance of hydrogen-bonded networks in regulating and enforcing proton transport. But while experimental studies concentrate on quantifying observable transient signals tied to intra-molecular motion, it is most desirable to test the validity of the measurements against theoretical models and often this is handled

using molecular simulations as basis. By itself, the study of the collective dynamics of water, in relation to the lifetime of hydrogen bonds, is a topic well explored in contemporary molecular simulations (Sutmann and Vallauri, 2002; Eaves et al., 2005; Laage and Hynes, 2006), with pioneering work performed by Stillinger and Raman in 1971 (Rahman and Stillinger, 1971). The provision for a faithful reproduction of the molecular properties of hydrogen bonded water molecules, of course, is that the representation of the liquid water system not only allow the correct reproduction of mechanical properties but also reflect the dissociative character of the O—H bond in water. The special requirement of simulations concerned with reactive phenomena such as proton transfer is the proper treatment of quantum effects necessary for dissociation of bonds, and although these have been modeled with considerable success through the use of polarizable models (Walbran and Komyshev, 2001; Brancato and Tuckerman, 2005; Harder et al., 2005), a digression into *ab initio* methods presents a more convenient alternative. Indeed, the empirical dependence of polarizable potentials entails a limited applicability to systems for which it has been optimized. *Ab initio* methods are often considered as a necessary sacrifice for accuracy relying mainly on a general treatment of electronic-structure problems particular to reactions<sup>2</sup>. Later, it will become apparent that *ab initio* methods offer a reliable means of abstracting the salient characteristics of proton dissociation, particularly in the vicinity of a strong charge, in a manner that is more implicit and more general than polarizable potentials.

## HYDROLYSIS OF METAL IONS

Aqueous solutions of metal ions offer simple yet valuable case systems, exposing much in terms of what the different properties of water mean for solvation phenomena, with little complication. The plethora of literature concerned with the elucidation of the hydration properties of different metal ions attest to this fact. In the case of stable hydrate

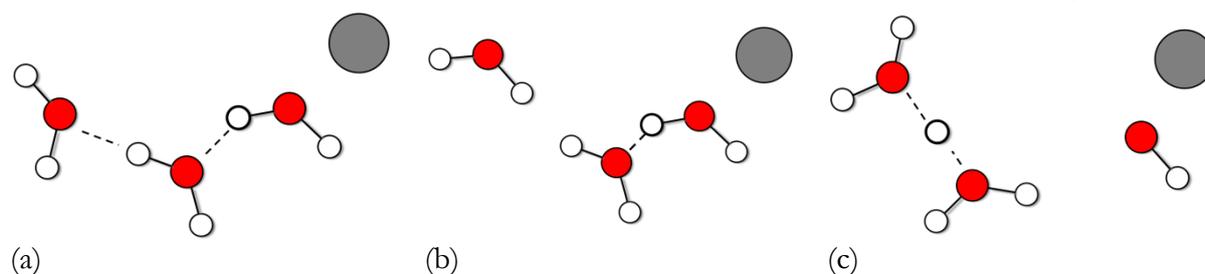
complexes, a high degree of short-range ordering of water molecules indicates the alignment of dipoles against the electric field surrounding the metal ion. Theoretical reproduction of such complexes, whether by condensed-phase simulations, or gas-phase modeling, is relatively trivial. In solution, long-range effects prescribe the correct treatment of Coulombic interactions. For shorter distances, faithful reproduction of N-body effects ensures the numerical stability of the simulations. Nevertheless, accurate description of these contributions to the total potential energy need only employ well-designed analytical functions provided that the concentration regime is dilute (i.e. the effect of a dense ionic atmosphere is removed).

While the structural features of the hydrate complex (e.g. metal—oxygen distances, coordination numbers, etc.) can be reproduced with significant confidence, reactive events, however infrequent (especially in the case of neutral solutions of metal ions), are completely neglected when using analytical force field potentials, and the simulation results are taken as the thermal averages observed in an actual experimental determination. The neglect of reactive processes may lead to significant errors in the case of small, highly charged metal ions in aqueous solution. The strong electric field with metal ions having a large charge-to-size ratio leads to an equivalently strong polarization of surrounding water molecules making it easier for protons to dissociate from their parent water molecule and leading to a decrease in pH of the solution. This, of course, is a simplistic way of describing the process of hydrolysis as several other competing reactions, dependent on concentration and temperature, may be present in solution (e.g. polymeric aggregation of hydrolyzed species, metal oxide precipitation, etc.) (Baes and Mesmer, 1976). Again, the problem may be reduced in the context of simulations by working in the limit of very dilute concentrations. Needless to say, if a molecular description of the process of hydrolysis is sought, then recourse to more exact treatments of polarization effects is

necessary. In so doing, forming a connection to the transport properties of a proton in liquid water becomes natural.

Coskuner and his co-workers (Coskuner et al., 2007) demonstrated the utility of Car-Parinello molecular dynamics (CPMD) (Car and Parinello, 1985) coupled with transition path sampling (TPS) (Dellago et al., 1998; Bolhuis et al., 1998) in elucidating the microscopic dynamics involved in the hydrolysis of water molecules in the vicinity of small trivalent metal ions:  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ . The study gives the first qualitative impression of hydrolysis: in the molecular level, dissociation of a proton from its parent (first shell) molecule occurs in the femtosecond timescale. This was later confirmed in the case of  $\text{As}^{3+}$  in the study made by Bhattacharjee and co-workers (Bhattacharjee et al., 2009), where the study instead involved the use of a hybrid quantum mechanical charge field molecular dynamics (QMCF-MD) (Rode et al., 2006). The “ultrafast” behavior of proton dissociation implies that, while related bulk properties (e.g. pH, pKa, and stability curves, etc.) may be relatively immune to fluctuations, hydrolysis in the molecular level may not, and a resort to theoretical methods is, therefore, mandatory to unravel its mechanism. The timescale of hydrolysis further provides the first connection to the anomalous mobility of a proton in liquid water, which, likewise, is too fast to be measured directly.

To see how hydrolysis can be characterized in the context of the Grotthuss mechanism,



**Figure 2.** The dissociation of proton from a first shell water molecule of the metal ion (grey) is part of (a) a hydrogen-bonding network that may extend up to the third hydration layer. (b) When the hydrogen bonds of the second shell water molecule with its neighbors in the succeeding shell are temporarily broken, the acceptor water molecule comes to its closest distance with the donor. (c) The free proton rapidly “hops” towards the bulk region by forming fleeting Zundel or Eigen complexes. Dashed lines indicate hydrogen-bonding.

transient structures in the simulation trajectories must be further scrutinized. Indeed, from the simulations of Coskuner et al., the dissociating proton was found to transition between Zundel and Eigen complex formation soon after leaving the first hydration shell of the metal ion, with energy profiles indicating a preference towards Zundel configurations. Thus, as far as theory is concerned, the fate of the dissociating proton can be modeled perfectly with the Grotthuss model. Naturally, one may contend that the strength of the electric field around the metal ion may be the primary factor at work in providing the energetic requisites for the breakage of the O—H bond of a first shell water molecule. In a more recent work by Lim and co-workers involving QMCF-MD simulations of tetravalent group 14 metal ions (Lim et al., 2010), it was suggested that the charge density of the metal ion only indirectly motivates the dissociation process. From close inspection of the simulation trajectories, it was shown that the dissociation of a proton from a donor water molecule in the first shell to an acceptor water molecule in the second shell is a process controlled by dynamics involving water molecules even up to the third hydration shell or the bulk solvent region. This effect is illustrated in Figure 2. This is not surprising if it is viewed in the context of the proton-hopping mechanism.

Earlier, it was noted that proton migration occurs along a bucketline consisting of a hydrogen-bonded network of water molecules. In a simulation study made by

Marx and his co-workers, proton-migration was seen to occur preferentially towards water molecules that have the most least number of H-bonded partners (Marx et al., 1999; Tuckerman et al., 2002). Thus, a bucketline of at least three water molecules would be involved in the proton migration. Because water molecules are in constant motion in the liquid state, thermal perturbations in the hydrogen-bonded network may be expected. These thermal fluctuations are very short-lived and identify the general relaxation of the system bath (the relaxation of the different modes of motion in liquid water). For example, the orientation motion of water molecules has a typical decay constant that can go to a sub-picosecond range (Gale et al., 1999; Keutsch and Saykally, 2001; Moilanen et al., 2008).

That proton migration occurs through hydrogen bonds that must consistently be guided towards acceptors having transiently depleted coordination environment has profound consequences in hydrolysis of metal ions. In order for a water molecule to be a qualified proton acceptor, it must have enough translational freedom to come to close contact with the donor (as in Figure 2b), which occurs only when it removes its hydrogen bonding with water molecules in the succeeding solvent region. This provides a connection between hydrolysis and the general features surrounding the structural diffusion of a proton in liquid water, both being governed by non-deterministic events and ultimately dependent on time evolution of many-body correlated motion.

## SUMMARY

In this review, we have shown how the conceptual mechanism of proton transport in liquid water relates to the hydrolysis of metal ions in aqueous solution. By and large, the Grothuss model gives the most physically viable explanation for the anomalous mobility of a proton in liquid water. It is, therefore, only fitting to identify the processes involved in the hydrolysis of metal ions under the same conceptual framework. It is not surprising that the process of proton dissociation in aqueous

media can be motivated by highly charged metal ions, but that it is controlled by collective dynamics spanning several water molecules is a profound observation that can only be gained from the proper application of theory in computational methods. Because the description of reaction pathways rely heavily on an accurate reflection of electronic-structure redistributions, *ab initio* methods prove to be a natural choice for studying the mechanism of proton transport in liquid water, and likewise for the hydrolysis of metal ions. From the implications of such studies discussed in this paper, and with further advances in the synergy of experiment and theory, a way of someday realizing a full understanding of bulk phenomena rooted on molecular effects is certainly attainable.

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