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Collective Tunneling | Very Important Paper

Exceptional Isotopic-Substitution Effect: Breakdown of Collective Proton Tunneling in Hexagonal Ice due to Partial Deuteration**

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Abstract: *Multiple proton transfer controls many chemical reactions in hydrogen-bonded networks. However, in contrast to well-understood single proton transfer, the mechanisms of correlated proton transfer and of correlated proton tunneling in particular have remained largely elusive. Herein, fully quantized ab initio simulations are used to investigate H/D isotopic-substitution effects on the mechanism of the collective tunneling of six protons within proton-ordered cyclic water hexamers that are contained in proton-disordered ice, a prototypical hydrogen-bonded network. At the transition state, isotopic substitution leads to a Zundel-like complex, [HO···D···OH], which localizes ionic defects and thus inhibits perfectly correlated proton tunneling. These insights into fundamental aspects of collective proton tunneling not only rationalize recent neutron-scattering experiments, but also stimulate investigations into multiple proton transfer in hydrogen-bonded networks much beyond ice.*

Single proton transfer is ubiquitous, and its mechanism in various environments is well understood,[1–7] even when tunneling is involved.[8,9] In contrast, multiple proton transfer is more complex, and its mechanism thus generally remains elusive. For example, double proton transfer occurs in a concerted fashion in the formic acid dimer,[10] but as a stepwise process in hydroporphyrins,[11] and, although the transfer of up to four protons has been studied,[12–17] it is unknown a priori whether multiple proton transfer is sequential or concerted.[17,18]

Multiple proton transfer involves light atoms; hence, tunneling and isotopic-substitution effects must be considered. An intriguing neutron-scattering study suggested the concerted tunneling of six protons in hexagonal ice[19] and unveiled the disappearance of the experimental signal upon partial deuteration: On average, only one protium (H) per six ring was substituted by deuterium (D).[19] Whereas quantum simulations indeed confirmed the collective tunneling of six protons at low temperature and revealed a transition to classical hopping at higher temperatures,[20] the enigmatic isotopic-substitution effect on this qualitatively new phenomenon, that is, correlated proton tunneling, has remained unresolved.

To unravel this effect, we herein used constrained quantum simulations to compare fully protonated with partially deuterated hexagonal ice, the so-called "H system" and "H/D system", respectively. At the transition state, this comparison reveals that charge defects in the H/D system localize near a Zundel-like complex, which is characterized by a symmetric hydrogen bond with the deuteron at its center, [HO···D···OH]. Partial deuteration of the H system thus leads to inequivalent protons, thereby destroying concerted proton tunneling. The intriguing isotopic-substitution effect on quantum fluctuations and collective tunneling unveiled herein explains the aforementioned experiments[19] and will guide future investigations into correlated multiple proton transfer in hydrogen-bonded systems.

To elucidate the loss of the experimental signal upon partial deuteration,[19] we performed quantum simulations of hexagonal ice containing either only protons (H system) or one deuteron per hexamer (H/D system), which are systems similar to those used in previously reported experiments.[19] Hexagonal ice consists of interconnected cyclic water hexamers and features quenched (static) proton disorder at low temperatures in the absence of defects, which causes the residual entropy.[21] Yet, a certain fraction of cyclic hexamers is proton-ordered for statistical reasons even in a proton-disordered ice crystal satisfying the ice rules,[21] i.e., the protons occupy equivalent positions along their respective hydrogen bonds, as schematically depicted in Figure 1. Proton-ordered cyclic hexamers are unique because the transfer of all six protons leads from the initial to the final state, both of which are defect-free. Hence, our computational model was based on such a proton-disordered hexagonal ice crystal (represented by 48 H_2O molecules in a periodic supercell subject to the ice rules) that contained one proton-ordered cyclic water hexamer within which collective proton transfer was investigated at 50 K.

To study isotopic-substitution effects, the H system, which comprised all thermal and quantum fluctuations, including zero-point motion, quantum delocalization, and tunneling, was compared to the H/D system, in which partial deuteration is described by classical, that is, infinitely heavy, particles to show the isotopic-substitution effect most clearly.[9,22] For completeness, the comparison of a fully deuterated model of hexagonal ice (D system), a classical reference, to the H system revealed quantum fluctuations. Furthermore, as multiple proton transfer in hexagonal ice is a rare event even in the deep-tunneling regime, it was induced by constraining

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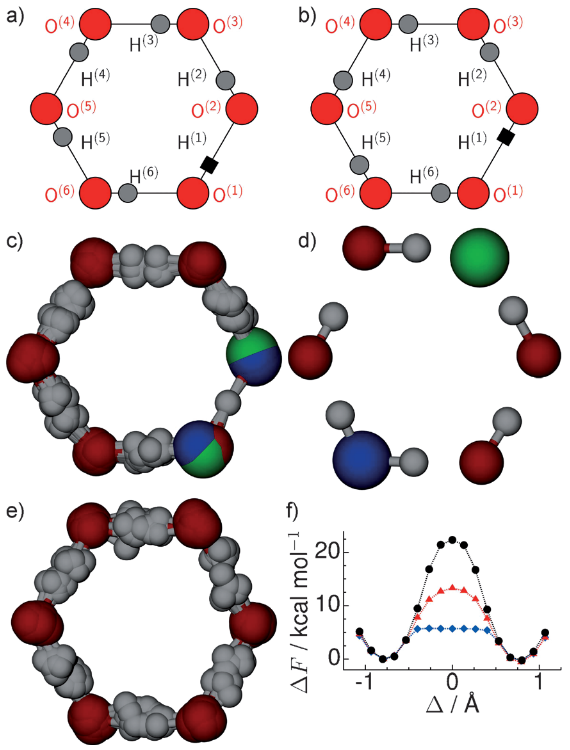

Figure 1. a, b) Top view of the initial (a) and final (b) states of the proton-ordered cyclic water hexamer embedded in a proton-disordered hexagonal ice crystal (consisting of 48 molecules subject to periodic boundary conditions, not shown for clarity). c–e) Representative transition-state configurations of the H/D (c), D (d), and H (e) systems. Oxygen and hydrogen atoms (a–e), and formal H_3O^+ and OH^- ionic defects (c, d) are shown in red, gray, blue, and green, respectively. The black square in (a) and (b) indicates the site of partial deuteration in the H/D system, and overlaid spheres represent quantum delocalization according to the usual path integral representation (c, e). f) Free energy profiles along the global proton-transfer coordinate $\varDelta = \sum \left[d\left(O^{(j)}H^{(j)}\right) - d\left(H^{(j)}O^{(j+1)}\right)\right]/6$, where $d(AB)$ is the distance between atoms A and B (H/D: ▲; D: ●; H: ◆).

the global proton-transfer coordinate $\varDelta = \sum \delta_j/6$, which serves as an approximate reaction coordinate and characterizes the collective transfer of six protons without imposing its concertedness, whereas the local proton-transfer coordinate $\delta_j = d(O^{(j)}H^{(j)})d(H^{(j)}O^{(j+1)})$ characterizes single proton transfer within hydrogen bond $j = 1,\ldots,6$ (see Figure 1 and Ref. [23] for details). The mechanism of correlated proton transfer for the H, H/D, and D systems was unraveled by analyzing the transition-state properties of the proton-ordered cyclic hexamer within the proton-disordered crystal environment. Here, the transition state is the maximum of the quantum free energy profile along the one-dimensional reaction coordinate Δ, as is usually the case for high-dimensional condensed-matter systems at finite temperature.

Representative transition-state configurations obtained from constrained ab initio molecular dynamics (D system: panel d) and ab initio path integral (H and H/D systems: panels e and c, respectively) simulations are depicted in Figure 1. The D system (Figure 1 d) contains a defect pair and localized deuterons; the H system exhibits no defects but six protons delocalized within each hydrogen bond owing to tunneling (Figure 1 e), which leads to local dynamic disorder through interconversion of the local proton-ordered hexamer configurations, whereas the H/D system (Figure 1) shows a unique feature: a symmetrized hydrogen bond centered around the deuteron. This [HO⋯D⋯OH] motif is reminiscent of the Zundel complex, where the H symbols here refer to the protons delocalized within neighboring hydrogen bonds in the proton-ordered hexamer. The qualitative differences in structure and defect type also correlate with the fraction of localized formal H_3O^+ and OH^- defects in the H/D, D, and H systems of approximately 16, 100, and 5%. As charge separation requires energy, the activation free energy of the H/D system lies in between those of the D and H systems (Figure 1 f), thus being a significant energy penalty to collective proton tunneling. Furthermore, the bell-shaped free energy profile of the H/D system differs qualitatively from that of the H system, thus requiring a mechanistic analysis.

According to the defect distribution among oxygen sites, which is shown in Figure 2, defects are localized at two opposite sites in the D system without any proton transfer (see Figure 3), whereas defects occur equally likely at all sites in the H system. In contrast, defects in the H/D system are preferentially found at the $O^{(1)}$ and $O^{(2)}$ sites, which form the Zundel-like complex [HO⋯D⋯OH] with the deuteron. Hence, the deuteron localizes defects and induces hydrogen-bond symmetrization, which is usually favored by nuclear quantum effects.

The indistinguishable δ_j distributions (Figure 3) of the H system indicate perfectly equivalent hydrogen bonds. In contrast, the δ_1 distribution of the H/D system, which reveals that the deuteron is close neither to the $O^{(1)}$ nor to the $O^{(2)}$ site, but resides in between and significantly perturbs the δ_2 and δ_6 distributions, differs strongly from the distributions of $\delta_{j\neq1}$, indicating the presence of inequivalent hydrogen bonds, which are due to the defect localization by the deuteron.

The influence of this inequivalence on collective proton transfer is revealed by the correlation between the local proton-transfer coordinates δ_1 and $\delta_{j\neq1}$ in Figure 4. No and perfect correlation between the proton motions exists in the D and H systems, as shown by the spherical and perfectly

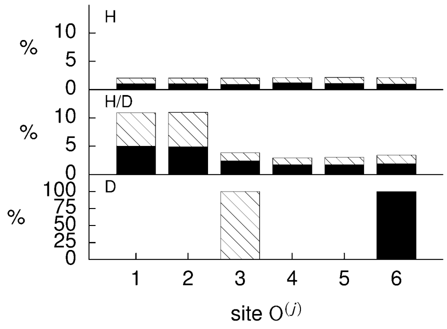

Figure 2. Probability of the oxygen site $O^{(j)}$ ($j = 1,\ldots, 6$) in the proton-ordered cyclic water hexamer that is embedded in a proton-disordered hexagonal ice crystal at the transition state to be the center of a formal H_3O^+ (filled) or OH^- (striped) defect for the H, H/D, and D systems (note the different scale for the D system). See Figure 1 for the labeling of hydrogen bond j.

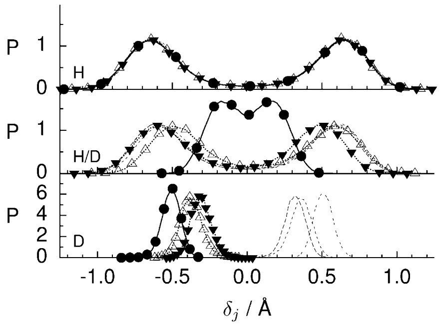

Figure 3. Distribution of the local proton-transfer coordinate δ_j for each hydrogen bond *j* within the proton-ordered cyclic water hexamer embedded in a proton-disordered hexagonal ice crystal at the transition state. See Figure 1 for the labeling of hydrogen bond *j*. δ_1: —— with ●; δ_2: ••••• with △; δ_3: -----; δ_4: -- --; δ_5: ——; δ_6: ••••• with ▼ for the H, H/D, and D systems; please note the different scale for the D system.

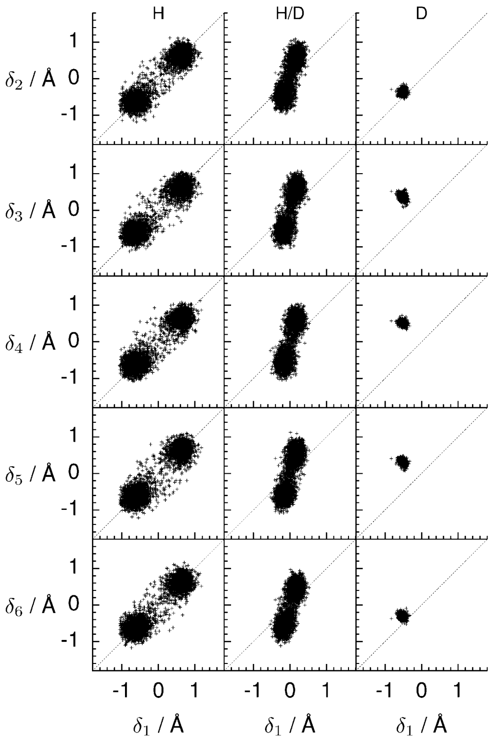

Figure 4. Correlation between the local proton-transfer coordinates $\delta_{j\neq1}$ ($j=2,\ldots,6$) and δ_1 within the proton-ordered cyclic water hexamer embedded in a proton-disordered hexagonal ice crystal at the transition state. See Figure 1 for the labeling of hydrogen bond *j*. The thin diagonal lines represent perfect correlation.

diagonal distributions, respectively. The correlation in the H system shows collective proton tunneling, which is characterized by a significant probability of finding protons at $\delta_j=0$ and across the full δ_j range (see Figure 3) for all six protons.[20] In stark contrast, the deuteron motion in the H/D system is negligibly correlated with the proton motion in the remaining hydrogen bonds, which cover the full $\delta_{j\neq1}$ range, whereas $\delta_1 \approx 0$ Å. Hence, although the protons exhibit uncorrelated single-particle tunneling after comparatively mild donor–acceptor compression (i.e., O–O contraction as discussed in Ref. [20], thus reducing charge separation), the deuteron in the H/D system localizes defects upon formation of the Zundel-like complex, thereby effectively destroying the collective proton tunneling of the six protons observed in the H system. This analysis explains the loss of the experimental signal in the related neutron-scattering study[19] upon partial deuteration, thus providing detailed insight into isotopic-substitution effects on collective proton transfer in hexagonal ice.

In summary, we have investigated the effects of isotopic substitution on collective proton tunneling by comparative quantum simulations of fully protonated and partially deuterated hexagonal ice. Compared with the protonated system, deuterons in proton-ordered cyclic water hexamers localize ionic defects in a Zundel-like complex, thus rendering hydrogen bonds inequivalent, destroying perfectly correlated collective proton tunneling, increasing the free energy barrier, and exponentially suppressing collective tunneling. These phenomena strongly differ from typical deuteration effects on single or double proton transfer and thus appear to be due to the collective nature of the underlying process. Hence, the influences of both temperature and isotopic substitution on collective proton tunneling, which were unveiled herein, should stimulate further studies of multiple proton transfer in hydrogen-bonded networks.

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[23] See the Supporting Information for methodological details.