

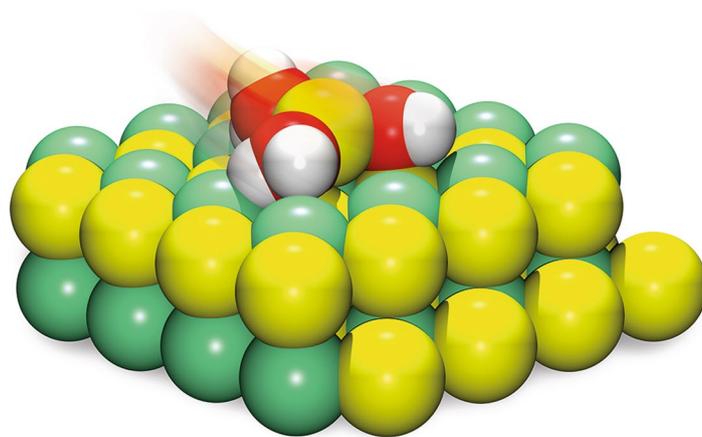
SURFACE CHEMISTRY

Ions surf across salt surface

“ This work provides new insights into the enhancement of ion conductivity in nanofluidics ”

The importance of molecular diffusion through narrow pathways — such as biological ion channels or nanofluidics — motivates the study of dynamics not only in solution but also across surfaces. Although scanning probe microscopy has allowed us to elucidate H₂O movement at surfaces, the transport of aquo complexes is less well understood. Writing in *Nature*, a consortium led by Li-Mei Xu, Yi Qin Gao, En-Ge Wang and Ying Jiang address this by describing in immaculate detail the structures and dynamics of [Na(D₂O)_{*n*}]⁺ complexes on a NaCl(001) surface.

Aquo complexes are difficult to study because they are labile yet can give rise to structural order beyond their inner coordination sphere. In contrast to the average structures of aquo complexes available from solution diffraction experiments, one can determine the structure of single aquo complexes on a surface using scanning probe microscopy. Jiang and colleagues used both ultrahigh resolution scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (AFM) to prepare and characterize the aquo complexes [Na(D₂O)_{*n*}]⁺ (*n* = 1–5). The team first condensed D₂O onto bilayer NaCl(001), which, in turn, sits atop a Au(111) substrate. Attaching a Cl[−] ion onto their microscope tip, they then took Na⁺ from the surface and constructed the aquo complexes by bringing the requisite D₂O ligands nearby. After these manipulations, the team replaced Cl[−] at the tip for CO, allowing them to image [Na(D₂O)_{*n*}]⁺ by weakly perturbative AFM. The CO-terminated tip and the polar D₂O ligands experience a quadrupolar electrostatic force, the short range of which enables submolecular resolution. Moreover,



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“the force is weak enough for the tip not to disturb the complexes,” explains Jiang. His team showed that low-coordinate mono-, di- and triaquo complexes preferentially localize between two Cl[−] ions on the surface, reflecting the high electrophilicity of [Na(D₂O)_{*n*}]⁺ when *n* = 1–3. In contrast, the Na⁺ centres in the tetra- and pentaquo complexes are less electrophilic and sit atop just one Cl[−]. Each complex adopts whichever of the two arrangements best satisfies demands of Na⁺ as well as its D₂O ligands, which bind surface Na⁺ and Cl[−] ions.

Characterizing the aquos required not only a weakly perturbative methodology, but also cryogenic temperatures. At 5 K, the low thermal energy of [Na(D₂O)_{*n*}]⁺ meant that when it came to studying dynamics, Jiang and colleagues had to excite the system by inelastic electron tunnelling, whereby hot holes or electrons are transferred to Au(111). The substrate then passes energy to [Na(D₂O)_{*n*}]⁺, populating D₂O bending modes and causing translation across NaCl(001). This motion is random if a CO-terminated tip is used, but proceeds towards the tip if it has Cl[−]. [Na(D₂O)₃]⁺ moves the fastest of all

the complexes, because although it bridges two surface Cl[−] ligands in its resting state, the barrier to accessing structures bound to one Cl[−] is only about 50 meV. Because the lower and higher hydrates overwhelmingly prefer dichlorido and monochlorido coordination, respectively, they have high barriers to translation and thus move only very slowly. Molecular dynamics simulations indicate that the movement of [Na(D₂O)₃]⁺ across NaCl(001) is even faster than the diffusion of Na⁺ through aqueous solution.

The high mobility of [Na(D₂O)₃]⁺ can also be attributed to a symmetry mismatch — the triaquo never feels quite at home at any place on the tetragonal surface. “This work provides new insights into the enhancement of ion conductivity in nanofluidics and suggests new ways to control this by engineering the symmetry of a surface,” states Jiang. The team is now studying different ions and surfaces to see just how general their symmetry mismatch concept is.

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ORIGINAL ARTICLE Peng, J. et al. The effect of hydration number on the interfacial transport of sodium ions. *Nature*. <https://doi.org/10.1038/s41586-018-0122-2> (2018)