Anomalous interfacial dynamics of single proton charges in binary aqueous solutions

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Our understanding of the dynamics of charge transfer between solid surfaces and liquid electrolytes has been hampered by the difficulties in obtaining interface, charge, and solvent-specific information at both high spatial and temporal resolution. Here, we measure at the single charge scale the dynamics of protons at the interface between an hBN crystal and binary mixtures of water and organic amphiphilic solvents (alcohols and acetone), evidencing a marked influence of solvation on interfacial dynamics. Applying single-molecule localization microscopy to emissive crystal defects, we observe correlated activation between adjacent ionizable surface defects, mediated by the transport of single excess protons along the solid/liquid interface. Solvent content has a nontrivial effect on interfacial dynamics, leading at intermediate water fraction to an increased surface diffusivity, as well as an increased affinity of the proton charges to the solid surface. Our measurements evidence the notable role of SMLM with single-particle tracking allows us to reveal single excess protons are transported in water along the H bonding network, further complexified at interfaces, with reports of self-assembly and specific adsorption of ions, which occur in the few layers of molecules at the interface between the solid surface and the solvent. While new insights have been obtained thanks to electokinetic measurements, second harmonic generation, dynamic atomic force microscopy, or time-resolved fluorescence, our fundamental understanding of the dynamics of these interfacial processes remains poor because of the difficulties in obtaining surface-specific information at both high spatial and temporal resolution. In this context, we could recently resolve the diffusive dynamics of individual excess proton charge at the interface between defected hexagonal boron nitride (hBN) and aqueous solutions. By allowing the direct observation of proton charge transport the single-molecule scale under various solvent conditions, the application of single-molecule localization microscopy (SMLM) to the reactive optically active defects hosted at the hBN crystal surface has the potential to bring new general insights on the dynamics and transport of charges at solid/liquid interfaces.

The physicochemical and charge solvation properties of the solvent are expected to have a strong yet poorly understood effect on interfacial charge dynamics. In aqueous media, one facile route to alter charge solvation and the hydrogen bonding structure is by mixing water with an organic amphiphilic solvent (e.g., acetone or alcohol such as methanol or ethanol) having both hydrophilic (polar—OH or ==O) and hydrophobic (apolar alkyl —CH3) moieties. These binary solutions show anomalous thermodynamic behavior in the bulk due to incomplete mixing at the molecular scale. The presence of hydrophilic alkyl groups hinders the participation of these organic molecules to the water hydrogen bonding networks and modifies its topology, an effect that has been probed extensively through molecular dynamics simulations and specific adsorption at hydrophobic surfaces.

Here, we investigate, at the single charge scale, the complex relationship between solvation and proton charge dynamics at solid/liquid interfaces. We use spectral SMLM to probe the interface between a defected hBN crystal and binary mixtures of water and organic solvents (methanol, ethanol, and acetone). By varying the relative amount of water in the mixtures, we fine-tune hydrogen bonding in the liquid and probe how it affects proton charge dynamics at the hBN surface. We first show that spectral SMLM can serve as a chemically sensitive probe of the surface state, allowing us to separate the photoluminescence signal due to the protonation of ionizable defects at the surface of the flake from the adsorption of the hydrophobic alkyl groups of the organic solvent, which leads to localized emission at a distinct wavelength. Combining spectral SMLM with single-particle tracking allows us to reveal single excess proton trajectories as a succession of jumps between surface defects, mediated by the transport of the solvated proton charge along the solid/liquid interface. We evidence nontrivial dynamics for these interfacial charges, characterized at intermediate water fraction, by an increase in interfacial diffusivity due to a reduction of the
desorption energy barrier of the proton out of the defects, as well as an increased affinity of the proton charge to the solid surface. Our measurements demonstrate the subtle role of solvation on interfacial proton charge dynamics and are rationalized through ab initio molecular dynamics simulations.

RESULTS

Spectral SMLM experimental setup

As shown in Fig. 1A, we use spectral SMLM to probe the dynamics of optically active defects at the surface of hBN crystals in contact with various aqueous and organic solvents. The samples are multilayer boron nitride flakes exfoliated from high-quality crystals (41). We induce a random distribution of surface defects on these exfoliated flakes through a brief plasma treatment (see the Supplementary Materials). Illuminating the hBN crystal with a 561-nm (2.21 eV) laser leads to the selective excitation of surface defects with energies well within the 6-eV bandgap of the material (Fig. 1A, green and red spots at the hBN surface), and a high–numerical aperture (NA) oil-immersion objective collects the resulting photoluminescence signal from 580 to 700 nm (i.e., 2.14 to 1.77 eV).

Optically active emitters present at the surface of the flake typically exhibit intermittent emission (blinking), leading to a sparse number of defects active on each frame. This sparse activation allows us to follow the dynamics of single defects using spectral SMLM techniques. Our superresolution setup, shown in Fig. 1A and described previously (42, 43), is augmented with the capability of spectral imaging, allowing us to localize individual defects with nanometric accuracy while measuring their spectral response. Briefly, we collect the wide-field photoluminescence originating from the flake's surface and project half of the intensity on part of an electron-multiplying charge-coupled device (EMCCD) camera frame [(i), spatial SMLM]. In this spatial channel (i), emission from individual defects leads to diffraction-limited spots on the camera, which we localize with subpixel accuracy with a localization uncertainty $\sigma \approx \sigma_{PSF} / \sqrt{N} \approx 10$ to 40 nm, where $\sigma_{PSF} \approx 150$ nm is the SD of the Gaussian fit of the emitter's intensity and $N$ is the number of photons emitted by the defect during one acquisition frame. The other half of the photoluminescence signal is sent through a dispersive prism and is projected back onto the other part of the camera frame, allowing the simultaneous measurement of the emission spectra of the bright individual emitters [(ii), spectral SMLM; see fig. S1].

Fig. 1. Spectral superresolution reveals chemical states of hBN surface defects. (A) Spectral SMLM setup with an hBN crystal in contact with the solvent. Colored dots represent photoluminescence signal emanating from single defects at the surface of the flake. The inset shows the chemical structure of pristine hBN flake (boron in blue and nitrogen in green). The photoluminescence signal emitted from the flake's surface is split into spatial (i) and spectral (ii) channels. In the spatial channel (i), emission from individual defects leads to diffraction-limited spots (highlighted by red boxes), localized with subpixel nanometric accuracy. In the spectral channel (ii) vertical dispersion by a prism allows the simultaneous measurement of the spectra of these individual emitters (highlighted by colored vertical lines). (B and C) Ensemble emission spectrum of hBN defects in contact with (B) water and (C) dodecane, showing two main emission lines with $\lambda_A \approx 585$ nm (2.08 eV) and $\lambda_B \approx 630$ nm (1.97 eV), respectively. Representative spectra from individual emitters are shown in the inset. In (B), emission $\lambda_A$ is due to the protonation-induced transition between non-emissive deprotonated defect $V_B^-$ and emissive protonated defect $V_BH^+$ with excited state $V_BH^{*}$. In the excited state, $V_BH^*$ can either relax radiatively to its ground state (green arrow) or undergo excited state proton transfer and relax back to $V_B^-$ (black arrow). a.u., arbitrary units. In (C), emission $\lambda_B$ is due to interaction of the apolar hydrophobic alkyl group (—CH$_3$) with defect $D_2$ (see the Supplementary Materials). Defect zero-phonon line is around 630 nm, and the second peak visible around 670 nm corresponds to the phonon sideband.

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Aqueous and organic solvents activate distinct types of defects

Hosted at the surface of the flake, defects react strongly with their environment. As reported previously (26), a small density of active defects is observed in air (typically ρ ≈ 10⁻³ defects μm⁻² frame⁻¹, with 20-ms exposure time). When the flakes are put in contact with solvents, the dynamics and density of activated defects increase markedly, pointing to the activation of defects by solvent molecules. Varying the solvent from aqueous to organic, we further observe that different solvents activate distinct types of defects. We compare in Fig. 1 (B and C) the spectral response of flakes in contact with water, where free protons H₃O⁺ are present in solution (Fig. 1B) and with dodecane, an organic hydrocarbon solvent (Fig. 1C), showing drastically different emission spectra depending on these two conditions and pointing to the activation of distinct emission lines.

For the case of the hBN flake in contact with water (Fig. 1B), the ensemble spectra are characterized by an emission peak centered around λₐ ≈ 585 nm (emission line A, green). Spectra from individual defects are shown in the inset. This emission line in hBN has been previously reported in a number of studies (26, 42, 44, 45). As represented in the green panel, we demonstrated in a previous report (26) that this emission line originates from defects in their protonated (acid) form, with the deprotonated (basic) defect being non-emissive. We attributed the emission to a protonated boron vacancy VₖH, with the on/off blinking behavior related to defect protonation/deprotonation through VₖH + H⁺ ↔ VₖH⁺. Note that while our observations are fully consistent with an optical transition associated with distinct protonation states (26), the chemical nature associated with this emission line is still under debate.

Consistent with the absence of free protons in dodecane, emission line A is absent on flakes in contact with this organic solvent (Fig. 1C). We observe instead the emission of emitters at a second emission wavelength, centered here around λ₈ ≈ 630 nm (emission line B, red). This emission line has been reported previously in hBN (44, 46–48) and corresponds to the activation of a defect of unknown chemical structure, which we denote as D₂. Anticipating the results below, this emission line is also observed for flakes in contact with other organic solvents (acetone, ethanol, and methanol), and we attribute this emission to the interaction of the defect with the non-polar hydrophobic alkyl groups of the organic solvent molecules. The dependence of this emission line on solvent polarity can be attributed to the interaction of the dipole of the defect in its excited state with the solvent (49) and is consistent with the slight observed redshift of the emission for increasing solvent polarity (fig. S6). The observation of such solvent-mediated activation of the emission should guide the identification of the chemical structure of the associated defect.

Interfacial adsorption and defect activity in binary aqueous solutions

Using the spectral signature of these emissive surface defects, we can probe how the physicochemical surface state of the hBN/liquid interface is affected by the presence of mixtures of water and amphiphilic organic solvents (methanol, ethanol, and acetone). We thus quantify the activity of defects under various proportions of water and organic solvents, characterized by the water volume fraction X_{H₂O} [−]. We show, in Fig. 2A, colored superresolved maps of active defects at the flake’s surface, along with their ensemble spectra in the inset, and, in Fig. 2B, a reconstructed local spatial density map of activated defects on a 1-μm² region at the surface of the flake (irrespective of defect spectral signature). Quantifying defect activity and spectral emission allows us to get a direct readout of the local chemical and charge state of surface defects as a function of bulk solvent composition, varying systematically the proportion of water and amphiphilic organic solvents in contact with the flake. As shown on the ensemble spectra in the insets of Fig. 2A, we observe, in all conditions, the presence of the λₐ = 585 nm green emission line, characterizing the presence of protonated boron vacancies (Fig. 1D). At low water content (X_{H₂O} ≤ 0.2 in Fig. 2A), we observe the appearance of the second emission line λ₈ = 630 nm, originating from the interaction of hydrophobic alkyl groups with surface defects D₂. While the dense and random distribution of defects present at the flake’s surface prevents us from cross-correlating the spatial distribution associated with each defect type, achieving better control of defect locations and densities might allow for such quantitative correlations.

To further characterize the variation of interfacial defect state with bulk solvent composition, we plot, in Fig. 2C, the fraction θₐ and θ₈ of protonated and alkyalted defects for decreasing water volume fraction X_{H₂O} and, in Fig. 2D, their absolute density ρₐ and ρ₈ (estimated as ρₐ = ρ_{tot} × ρ_{H₃O⁺} with ρ_{tot} being the total density of localized defects per frame). As quantified in Fig. 2C and schematically represented in Fig. 2D, the density of protonated boron vacancies ρₐ first increases with decreasing water content, from 7.10⁻³ μm⁻² frame⁻¹ s⁻¹ in pure water (Fig. 2E, i) to a maximum of 1.310⁻² μm⁻² frame⁻¹ s⁻¹ in 60% water (Fig. 2E, ii), pointing to an increased surface affinity of proton charges to the hBN surface in these mixed solvent conditions. Further decreasing water content below X_{H₂O} = 0.2 leads to the activation of the second defect type D₂ due to the interaction with the hydrophobic alkyl groups of the organic solvent, as schematically represented in Fig. 2D. These observations are reported here for a mixture of water and acetone, but these trends are observed for the three organic solvents, with intrinsic variability when comparing individual flakes, due to local variation of the surface state (see fig. S5).

Spatiotemporal correlations and single proton charge tracking

Using the first type of defect as a marker for protonation events (Fig. 1B), we can then track and follow the dynamics of excess protons moving at the solid/liquid interface with single charge resolution. We restrict our analysis to the steady-state regime emerging under continuous illumination, where the surface concentration of active defects is constant (see fig. S4). Considering the condition X_{H₂O} = 0.6, we reconstruct, in Fig. 3A, a spatiotemporal plot of the activated defects in a 10-μm-by-10-μm area, with localized defects color coded with increasing time along the vertical axis. Note that, in this particular condition, only protonated defects are active at the surface of the flake (Fig. 2B), such that defect activation is indeed solely due to the dynamics of proton charges.

As shown in Fig. 3A, we see clear correlations in the activation of nearby defects over successive frames. Some of these spatiotemporal trajectories are highlighted in red and shown in Fig. 3B. As defects are emissive in their protonated form, these trajectories correspond to the successive activation of nearby defects by a single excess proton hopping from defect to defect (26) and successively activating
the fluorescence signal. The fact that we can observe such correlated trajectories demonstrates that after desorbing from a defect, the solvated proton charge has a pronounced tendency to move along the solid/liquid interface, leading to the activation of a nearby defect site. This affinity of the solvated proton charge to the hBN solid surface is thus at the root of these observed spatiotemporal correlations.

**DISCUSSION**

**Anomalous charge transport in mixtures**

Analyzing charge trajectories for various bulk solvent composition, we highlight, in Fig. 4A, representative trajectories observed at the flake’s surface for the three water volume fraction $X_{H2O} = 1, 0.8$, and 0.6, showing that the relative proportion of water and organic solvent has a marked effect on interfacial charge dynamics at the solid/liquid hBN interface. As we cannot attribute any spectra to low intensity defects (fig. S1), we track and follow activated defects indistinctively of their emission spectra. Down to $X_{H2O} = 0.4$, these active emitters correspond solely to protonated defects (Fig. 2C, green), while for smaller water fraction, the localized emitters and the corresponding interfacial dynamics are characteristic of both protonated and alkylated defects.

Focusing first on the conditions for which only protonated defects are present at the surface of the flake, we plot, in Fig. 4B, the evolution of the mean square displacement $MSD = \langle (x(t) - x(0))^2 \rangle$ observed over all trajectories $x(t)$ (see the Supplementary Materials). From the initial increase of the MSD with time, we extract an effective surface diffusion coefficient $D (m^2 s^{-1})$ as $MSD \approx 4D_t$, which we report in Fig. 4C for decreasing water fraction. As shown in this figure, we observe a 20-fold increase in $D$, from $D \approx 10^{-14} m^2 s^{-1}$ in pure aqueous solution to $D \approx 2.10^{-13} m^2 s^{-1}$ at intermediate water
fraction \(X_{\text{H}_2\text{O}} = 0.6\). The diffusion coefficient further decreases when reaching lower fraction of water (note that in the conditions of low water fraction \(X_{\text{H}_2\text{O}} < 0.4\), the effective diffusion coefficient and observed time traces would characterize interfacial mobility of both water and organic solvent molecules). This measured value \(D \approx 10^{-13} \text{ to } 10^{-14} \text{ m}^2 \text{ s}^{-1}\) for the interfacial proton diffusion coefficient is five to six orders of magnitude lower than the bulk proton diffusion coefficient \(D_{\text{bulk}} \approx 10^{-8} \text{ m}^2 \text{ s}^{-1}\), consistent with a surface transport limited by the desorption of proton charges out of the defects (26). Expressing the surface diffusion coefficient \(D\), as an activated desorption-limited process, we can write \(D \sim e^{-\Delta F_{\text{defect}}/kT} \cdot v_0 \cdot a^2\), with \(v_0 \approx 1 \text{ GHz}\) being a characteristic attempt frequency, \(a \approx 10 \text{ to } 100 \text{ nm}\) being a characteristic interdefect distance, and \(\Delta F_{\text{defect}}\) being a free energy desorption barrier. The 20-fold increase in interfacial mobility at intermediate water concentration would then correspond to a net decrease of the desorption barrier by \(3 k_B T\) or \(77 \text{ meV}\). In pure water, taking \(D \approx 10^{-14} \text{ m}^2 \text{ s}^{-1}\), the mean desorption free energy is estimated to be of the order of \(0.4 \text{ to } 0.5 \text{ eV}\).

**Elementary steps during proton surface transport**

Because we can access the details of the trajectories at the single-molecule scale, we are able to further investigate interfacial proton charge dynamics. We can thus disentangle the various elementary steps at play during proton surface transport, i.e., the desorption of the proton out of the defect site, the transport of the solvated proton charge along the solid/liquid interface to the next defect, and the irreversible desorption of the proton out in the bulk. Analyzing these random walks, we extract, in Fig. 4 (D and E), both the residence time at each defect site (merging uncertainty-limited localizations as one site) and the number of visited defects along a single trajectory (see the Supplementary Materials).

We first show, in Fig. 4D, the distribution of residence time on the defects when the flake is in contact with aqueous solutions (blue, \(X_{\text{H}_2\text{O}} = 1\)) and at intermediate water fraction (green, \(X_{\text{H}_2\text{O}} = 0.6\)). These distributions follow power law scaling (dashed lines with slope \(-2\) and \(-3.8\)), and we observe a steeper distribution of residence time for \(X_{\text{H}_2\text{O}} = 0.6\) (comparing green and blue curves), consistent with the fact that the increase in the effective surface diffusion observed at intermediate water concentration is due to the facilitated proton desorption out of the defects, leading to a reduced residence time on the defect sites.

A major observation relates to the correlation in the activation of adjacent defect sites, demonstrating the affinity of the solvated proton charge to the solid/liquid interface. To analyze this effect in more detail, we plot, in Fig. 4E, the distribution of the number of defects visited during a single trajectory for various water fractions. The number of visited defects is distributed approximately exponentially and follows the same nonmonotonic trend as the diffusion coefficient, with a maximum in the number of visited defects at intermediate water fraction (Fig. 4E, green). These observations are consistent with the large and homogenous activation of defects observed at the flake’s surface at intermediate water fraction (Fig. 2, A and B) and indicate an increased affinity of the proton charges to the solid surface due to either an increased affinity of the solvated charge to the pristine surface during the transport between adjacent defects or an increased probability of readsorption to the surrounding surface defects. Last, at low water fraction, the number of visited defects decreases, which would indicate an altered interaction of the proton with the defect-free part of the crystal. Note, however, that in these conditions, another type of defect is also active at the surface because of hydrophobic interaction with the solvent, making the distinction of the dynamics between protonated and alkylated defects difficult.
To analyze more quantitatively this segregation of the proton charges at the interface, we follow previous ensemble observations (50, 51) and assume the presence of a free energy barrier $\Delta G$ (eV) responsible for the trapping of the solvated proton charge at the interface between the hBN and the solvent during transport between adjacent defects. The presence of this barrier would lead to a characteristic time scale $t_{\text{escape}} \approx 1/v_1 \cdot e^{\Delta G/kT}$ for the escape of the solvated proton out of the pristine interface, with $v_1 \approx 10^{13}$ s$^{-1}$ being the typical frequency for rate processes at surfaces (50). Assuming that the proton diffuses from one defect to the other following a bidimensional random walk with a diffusion coefficient of the order of its bulk value $D_{\text{bulk}} \approx 10^{-8}$ m$^2$ s$^{-1}$, we can also express the characteristic time for transport between adjacent sites as $t_{\text{diff}} \approx a^2/4D_{\text{bulk}} \approx 2.5$ to 250 ns, with $a \approx 10$ to 100 nm being the characteristic interdefect distance. The distribution in the number $N$ of defects visited by individual protons can then be expressed as $P(N) \approx e^{-N/1 N_1}$, with $N_1 \approx t_{\text{escape}}/t_{\text{diff}}$. For $X_{\text{H}_2\text{O}} = 0.6$, we estimate $N_1 \approx 3.3$ (Fig. 4E), and the associated free energy barrier $AG$ can then be expressed as $\Delta G = kT \cdot \log \left( a^2 v_1 \right) - 4D_{\text{bulk}} \cdot N_1 \approx 11$ to 16 kT $\approx 0.3$ to 0.4 eV. Although coarse, this estimation is in fair agreement with the free energy barrier for proton trapping at pristine interfaces obtained from simulations, ranging from 0.15 to 0.3 eV (fig. S10). Note, however, that our simulations rather show a monotonic decrease of the affinity of the proton charge to the pristine surface for decreasing water content.

**Simulation**

To probe mechanistically the kinetic factors affecting proton charge dynamics, we turn in Fig. 5 to ab initio simulations of the reactivity of the negatively charged boron vacancies. We show, in Fig. 5A, the simulation cell composed of a mixture of water and methanol molecules interacting with the hBN surface. Water/methanol mixture was considered for the simulations, as methanol represents the simplest organic chemical species having an amphiphilic character due to its hydrophobic $\text{─CH}_3$ and its hydrophilic $\text{─OH}$ and is thus a good model system to understand the behavior of potentially more complex water/ethanol and water/acetonitrile mixtures.

As shown in Fig. 5B, we compute the energy barrier for the transfer of proton from the $\text{H}_3\text{O}^+$ cation to the negatively charged boron vacancy $V_{\text{B}}$ (see the Supplementary Materials). Varying, as shown in Fig. 5C, the first solvation shell of the hydronium from (i) two water, (ii) one water and one methanol, to (iii) two methanol molecules, we extract from these simulations the enthalpic desorption energy barrier for defects in the ground state (blue, $\Delta E_{\text{GS}}$) and excited state (red, $\Delta E_{\text{ES}}$), respectively.

As reported in Fig. 5C, our simulations evidence a reduction of the enthalpic energy desorption barrier $\Delta E_{\text{GS}}$ and $\Delta E_{\text{ES}}$ by $\sim 120$ and $\sim 200$ meV, respectively, when a single methanol molecule is present in the hydronium solvation shell, in qualitative agreement with the large increase in diffusion coefficient observed in Fig. 4C at intermediate water concentration. Note that the total free energy barrier $\Delta F_{\text{GS}}$ for proton desorption will be further reduced by a constant entropic contribution of $\sim 0.5$ eV in the three conditions (i to iii) and might further decrease in mixture because of their anomalous mixing entropy (see the Supplementary Materials) (52). On the contrary, the free energy barrier for proton adsorption shows a smaller increase of 40 to 120 meV at intermediate water concentration (see the Supplementary Materials), which would suggest that the increased number of visited defects evidenced in Fig. 4E is indeed due to an enhanced affinity of the solvated charge to the solid surface rather than an increased readsorption probability at the defect site.

To interpret mechanistically this change in the desorption barrier out of the defect, we analyzed the charge density of the solvating molecules for the various compositions of the solvation shells (fig. S9). We observe that when methanol is present in the first solvation shell of the hydronium ion, its large electron cloud leads to an...
increase in the electron density on the central oxygen of the aqueous core of the hydronium ion, rationalizing the observed decrease in the desorption barrier of H⁺ at intermediate water concentration. This effect is consistent with previous analysis (38).

Comparing desorption energy for defects in the ground state and excited state, respectively (Fig. 5, B and C, comparing red and blue), we also find a 0.6 eV reduction of the desorption energy barrier for a defect in the excited state, consistent with our experimental observations that proton dissociation is favored under illumination (fig. S4) (26). The inset of Fig. 5B shows the difference in electron density between the excited and the ground state, evidencing a positive charge density difference around the defect in its excited state, consistent with a higher electrostatic repulsion leading to a net decrease of the desorption barrier. However, note that a quantitative agreement between the absolute computed desorption energy barrier and our experimentally measured diffusion coefficient is out of reach of these simulations. This could be due to either an incorrect defect type, with a less electron-negative defect that would indeed decrease the desorption barrier, or the fact that photoexcitation could lead to an excited state with higher energy, distinct from the one considered in this simulation.

Applying spectral SMLM to defected hBN crystals in contact with binary mixtures of water and organic solvents, we investigated at the single proton scale, the complex relationship between solvation and charge dynamics at solid/liquid interfaces. We evidenced a nontrivial dynamics of interfacial proton charges with solvent content, characterized at intermediate water concentration by an increased interfacial diffusivity due to a reduced desorption energy barrier of the charge out of the defects, concomitant with an increased affinity of the charge to the solid surface. Our measurements, corroborated by ab initio simulations, demonstrate the subtle role of solvation on interfacial proton charge dynamics and further establish the potential of SMLM for the investigation of a wide range of dynamic processes at solid/liquid interfaces.

**MATERIALS AND METHODS**

**Spectral SMLM setup and imaging conditions**

Imaging was performed using a home-built spectral SMLM setup described previously (42). Briefly, the sample is excited using a 561-nm laser (Monolithic Laser Combiner 400B, Agilent Technologies). The excitation beam from the laser is focused on the back focal plane of an oil-immersion 100× objective (Olympus TIRFM 100X, 1.45 NA), leading to the wide-field illumination of the sample. Photoluminescence signal from the sample is collected by the same objective and filtered using dichroic and emission filters (ZT488/561rpc-UF1 and ZET488/561m, Chroma). Emission is further split in two “spatial” and “spectral” paths using a beam splitter. As described in (53), these two paths consist of two telescopes, sharing one lens and with a magnification factor of 1.6 and 1.4, respectively. Lenses are achromatic doublet lenses (Qioptiq). A prism (PS863, Thorlabs) is placed in the spectral path at the Fourier plane and at the angle of minimum deviation. Spatial and spectral images of the sample are then projected on an EMCCD camera (Andor iXon Life 897), with a back projected pixel size of 100 nm in the spatial channel. In the spectral channel, the prism leads to a vertical shift and dispersion of the emitter position equal to 0.25 pixel/nm. The camera is operated with an electron-multiplying gain of 150 and sampling time of 20 ms. Illumination power, as measured at the back focal plane of the objective, is set to 44 or 60 mW, corresponding to power densities of 2.2 to 3 kW cm⁻². The sample is mounted on a piezoelectric scanner (Nano-Drive, Mad City Labs) to compensate for vertical drift using an infrared-based feedback loop.

**Sample preparation and buffer solutions**

hBN multilayer flakes are exfoliated from high-quality bulk crystals (41) on glass coverslips (#1.5 micro cover glass; 25 mm in diameter; Electron Microscopy Sciences). Homogeneous distribution of defects at the surface of the flake are induced by submitting the flake to a low-power oxygen plasma treatment [100 mW, 30 sccm (standard cubic centimeters per minute) O₂ flow] ranging from 10 to 60 s. Binary solvent mixtures are obtained by mixing deionized (DI) water (pH 5.5) with methanol (99.8% purity; Sigma-Aldrich), ethanol (99% purity; Sigma-Aldrich), and acetone (99.5% purity; Sigma-Aldrich). Experiments in pure aqueous solutions were carried out using either DI water (pH 5.5) or water solutions buffered with 100 mM KCl at pH 3 (adjusted using HCl). Upon interaction of the hBN flakes with concentrated or pure solutions of organic solvent, we
observe irreversible change of the surface state (the original state is not recovered when going back to pure water) and slow aging (fig. S1). Experiments in binary mixtures at various water volume fraction are thus performed by progressively increasing the concentration of organic solvent in the mixtures.

**SMLM data analysis**

Emitters in the spatial channels and peak emission spectra in the spectral channels are localized using the ImageJ plugin Thunder- STORM (54). Briefly, a wavelet filter is applied to each frame. Peaks are then fitted by two-dimensional integrated Gaussians. In the spatial channel, only emitters with intensity larger than the SD of the first wavelet level are considered. This localization procedure allows us to obtain localization tables for the spatial positions of active emitters at the surface of the flake at each time frame. Localization precision $\sigma$ for least square estimate is calculated on the basis of the Thompson-Larson-Webb formula (55). The leading order in localization precision scales as $\sigma_{xy} = \sigma_{PSF}/\sqrt{N}$, where $\sigma_{PSF} \approx 150$ nm is the SD of the Gaussian fit of emitter’s intensity (corresponding to a diffraction-limited spot fixed by the point spread function with a full width at half maximum of $\sim 350$ nm) and $N$ is the number of photons emitted by the defect during the acquisition of one frame. We obtain an average localization precision around 20 nm.

Spectral assignment of emitters in the spatial channel is obtained by computing the projected position of emitters in the spectral channel for a fixed emission wavelength of 650 nm and performing a pair-search algorithm to find the closest spectral peak localization in a vertically elongated rectangular zone around their image. Full spectra in Fig. 1 are obtained by averaging the spectrum of single emitters over all frames for which spectral assignment is successful. As shown in Fig. S2, the spectra of individual defects are obtained preferentially for the brighter surface defects.

**Trajectory analysis**

Charge trajectories at the surface of the flake were analyzed using single-particle tracking techniques as described in a previous work (26) using the available online tracking algorithm (http://site.physics.georgetown.edu/matlab/). Briefly, emitters are first localized as described above. Active sites are then identified as belonging to the same trajectory when present in two consecutive frames within a user-defined threshold distance $d \approx 300$ nm [unambiguously defined from the distribution of step length $\delta t$; see (26)]. For most conditions, this threshold is small compared to the typical distance between active sites on a single frame, allowing to consistently extract the trajectories. When the surface concentration of active sites becomes too large (typically larger than 0.5 $\mu$m$^{-2}$ frame$^{-1}$, leading to an average interdefect distance of 0.8 nm), spurious correlations between nearby sites lead to false trajectory assignment, and we discard these conditions.

The ensemble diffusion coefficient is then obtained through a linear fit of the initial increase of the MSD with time (26). This MSD can be computed by restricting the average on trajectories larger than a threshold length $N_t$. For low density of defects and large diffusion coefficient, the obtained MSD is independent of this threshold trajectory length. In the opposite conditions of low diffusion coefficient and large defect density, spurious correlations between randomly activating defects lead to an overestimation of the MSD at short times [see (26)]. For consistency in our analysis, we thus systematically compute the MSD with $10 \leq N_t \leq 15$ and report the variation in the measured diffusion coefficient over this range of threshold length as error bars.

To obtain the distribution of residence time on each defect site (Fig. 4D) and the number of defects visited along a given trajectory (Fig. 4E), successive localizations along the trajectories are merged when they are within a defined distance corresponding to twice their localization uncertainty.

**Simulation**

The barrier calculations are performed by a self-consistent analysis of the density functional theory (DFT) (56) using the Vienna ab initio simulation (VASP) package (57, 58). The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (59), which comes under the generalized gradient approximation (GGA), was used, and projected augmented wave pseudopotentials with a 400-eV energy cutoff and Gamma point–centered k-point of $4 \times 4 \times 4$ were used. The barrier for H$_2$O$^+$ and V$_{\text{hBN}}$ is calculated by slowly moving the proton away from the water molecule and toward the surface with the system shown in Fig. 5A. Each unit cell consists of 42 molecules of H$_2$O and 1 molecule of H$_2$O$^+$ placed on an hBN surface with a negatively charged boron vacancy (V$_{\text{hBN}}$). The simulation box has dimensions of 10.0182 Å by 8.676 Å by 30 Å. In the simulations of mixtures, an additional 20 molecules of methanol are added to the system to ensure a 50% by volume mixture of methanol-water. All the structures are relaxed using an energy convergence criterion of $10^{-6}$ eV. The entropic barriers are calculated using standard statistical mechanics (60) and are independent of the molecules in the first coordination shell (see the Supplementary Materials).

For calculating the energy barrier in the excited state, the band energy diagram of a boron vacancy on hBN is first evaluated from the eigenvalues of the ground state in VASP using the PBE potential. Next, the occupancies of the electrons in the excited state are set using the constrained GGA approach (61). The occupancies are set in such a way that one electron is excited to its first excited state (defect state 1 in fig. S7). Last, the self-consistent calculations are repeated to calculate the static energy barriers for the excited state with the same procedure as the barrier calculations of the ground state.

To study the interfacial free energy profile of a hydronium ion in water–methanol mixtures, molecular dynamics simulations were performed using LAMMPS (62) for pure water, methanol, and 50% methanol-water mixture. The free energies were obtained from the potential of mean force and through umbrella sampling of multiple simulations. The system consists of 128 atoms on the hBN surface and 1 H$_2$O$^+$ molecule, with the pure water system having 344 water molecules, pure methanol having 160 methanol molecules, and 50% methanol system having 178 water and 80 methanol molecules. For calculating the free energy of a hydronium ion in water–methanol mixtures, molecular dynamics simulations were performed using LAMMPS (62) for pure water, methanol, and 50% methanol-water mixture. The free energies were obtained from the potential of mean force and through umbrella sampling of multiple simulations. The system consists of 128 atoms on the hBN surface and 1 H$_2$O$^+$ molecule, with the pure water system having 344 water molecules, pure methanol having 160 methanol molecules, and 50% methanol system having 178 water and 80 methanol molecules. The liquid mixtures are placed on the hBN surface, with the dimension of the simulation box being 20.036364 Å by 17.352 Å by 80 Å and a canonical ensemble is used at 300 K. The Lenard-Jones parameters used for B, N, and O in the molecular dynamics simulations have been taken from (63), and C–C interactions were taken from (64). The remaining interactions were estimated through the Lorentz-Berthelot mixing rules. The bonding parameters for water and methanol were taken from SPC/E (65) and OPLS/AA (66) potential models of water and methanol, respectively. The simulations for fig. S10 are equilibrated for 2 ns, and the data are collected in the production run of 5 ns.
SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.8b5868

REFERENCES AND NOTES
1. M. Bränden, T. Sanden, P. Brzezinski, J. Widengren, Localized proton microcircuits at the biological membrane–water interface. *Proc. Natl. Acad. Sci. U.S.A.* 103, 19766–19770 (2006).
2. S. Serowy, S. M. Saporov, Y. N. Antonenko, W. Kozlowski, V. Hagen, P. Pohl, Structural proton diffusion along lipid bilayers. *Biophys. J.* 84, 1031–1037 (2003).
3. C. Zoplin-Daumet, H. H. Xu, A. Esfandiar, M. Lozada-Hidalgo, C. F. Wang, Q. Yang, A. V. Tyurinu, A. Keerthi, B. Radha, A. K. Geim, Complete steric exclusion of ions and proton transport through confined monolayer water. *Science* 363, 145–148 (2019).
4. K. G. Zhou, K. S. Vasu, C. T. Cherian, M. Neek-Amal, J. C. Zhang, H. Ghorbanfekal-Kalashmi, K. Huang, O. P. Marshall, V. G. Kravets, J. Abraham, Y. Su, A. N. Grigorenko, A. Pratt, A. K. Geim, F. M. Peeters, K. S. Novoselov, R. R. Nair, Electrically controlled water permeation through graphene oxide membranes. *Nature* 559, 236–240 (2018).
5. Z. Zhang, X. Li, J. Yin, Y. Xu, W. Fei, M. Xue, Q. Wang, J. Zhou, W. Guo, Emerging hydrovoltaic technology. *Nat. Nanotechnol.* 13, 1109–1119 (2018).
6. A. Sinia, M. L. Bocquet, L. Bocquet, New avenues for the large-scale harvesting of blue energy. *Nature Rev. Chem.* 1, 0091 (2017).
7. X. Qian, L. Chen, Y. Liu, S. Lui, S. Fei, L. G. Hou, S. Chen, L. Song, K. H. Thebo, H.-M. Cheng, W. Ren, CdPS 3 nanosheets-based membrane with high proton conductivity enabled by Cd vacancies. *Sci. Adv.* 8, 2021.02.19 (2022).
8. A. Michaelides, P. Hu, Catalytic water formation on platinum: A first-principles study. *J. Am. Chem. Soc.* 132, 4233–4242 (2011).
9. W. Kann, C. Spreafico, A. Kleibert, J. Gobrecht, J. Vandevendele, Y. Ekinh, J. A. Van Bokhoven, Catalytic support effects on hydrogen spillover. *Nature* 541, 68–71 (2017).
10. S. Stehle, A. S. Braeuer, Hydrogen bond networks in binary mixtures of water and organic solutions studied by soft x-ray absorption spectroscopy. *J. Phys. Chem. B.* 116, 7698–7726 (2012).
11. M. K. Petersen, G. A. Voth, Amphiphilic character of the hydrated proton in methanol-water mixtures. *J. Phys. Chem. B.* 110, 7085–7089 (2006).
12. K. Voitovvsky, D. Goffe, J. J. Segura, F. Stellacci, M. Ceriotti, Thermally-nucleated self-assembly of water and alcohol into stable structures at hydrophobic interfaces. *Nat. Commun.* 7, 13064 (2016).
13. M. A. Halm, V. Kohn, A. Michaelides, L. Collod, The role of water structure in the solvation of ions. *Nat. Rev. Mol. Cell Biol.* 18, 78–91 (2017).
14. T. Taniguchi, K. Watanabe, T. Maruyama, K. Watanabe, A. Radenovic, Wide-field spectral super-resolution mapping of optically active defects in hexagonal boron nitride. *Nano Lett.* 19, 2516–2523 (2019).
15. J. Feng, H. Deschout, S. Caneva, I. Lon, P. Lazic, A. Radenovic, S. Hofmann, I. Lončarić, P. Lazic, A. Radenovic, Imaging of optically active defects with nanometer resolution. *Nano Lett.* 18, 1739–1744 (2018).
16. L. J. Martínez, T. Pelini, W. Waselowski, J. R. Maze, B. Gil, G. Cassabois, V. Jacques, Efficient single photon emission from a high-purity hexagonal boron nitride crystal. *Phys. Rev. B.* 94, 121405 (2016).
17. G. Grosso, H. Moon, B. Lienhard, S. Ali, D. F. Efetov, M. Furchi, J. R. Herrero, M. J. Ford, I. Aharonovich, D. Englund, Tunable and high-purity room temperature single-photon emission from atomic defects in hexagonal boron nitride. *Nat. Commun.* 8, 705 (2017).
18. F. Hayee, L. Yu, J. Z. Zhang, C. J. Ciccario, M. Nguyen, A. F. Marshall, I. Aharonovich, J. Vuikkov, P. Narang, T. F. Heinz, J. A. Dionne, Revealing multiple classes of stable quantum emitters in hexagonal boron nitride with correlated optical and electron microscopy. *Nat. Mater.* 19, 534–539 (2020).
19. S. Choi, T. T. Tran, C. Elbadawi, C. Lobo, X. Wang, S. Juodkazis, G. Senutinas, M. Toth, I. Aharonovich, Engineering and localization of quantum emitters in large hexagonal boron nitride layers. *ACS Appl. Mater. Interfaces* 8, 29642–29648 (2016).
20. T. T. Tran, C. Elbadawi, D. Totonjian, C. J. Lobo, G. Q. Grosso, H. Moon, D. R. Englund, M. J. Ford, I. Aharonovich, M. Toth, Robust multicolor single photon emission from point defects in hexagonal boron nitride. *ACS Nano* 10, 7331–7338 (2016).
21. A. S. Klymchenko, Solvatochromic and fluorostructural dyes as environment-sensitive probes: Design and biological applications. *Acc. Chem. Res.* 50, 366–375 (2017).
22. E. Weichselbaum, M. Osterbauer, D. G. Knyazev, O. V. Batischev, S. A. Akimov, T. Hai Nguyen, C. Zhang, G. Knorr, N. Agmon, P. Carloni, P. Pohl, Origin of proton affinity and ionization potential for carbon nitride. *Nano Lett.* 19, 2516–2523 (2019).
23. S. Choi, T. T. Tran, C. Elbadawi, C. Lobo, X. Wang, S. Juodkazis, G. Senutinas, M. Toth, I. Aharonovich, Engineering and localization of quantum emitters in large hexagonal boron nitride layers. *ACS Appl. Mater. Interfaces* 8, 29642–29648 (2016).
24. R. F. Lama, B. C. Y. Lu, Excess thermodynamic properties of aqueous alcohol solutions. *J. Chem. Eng. Data* 10, 216–219 (1965).
25. R. Yan, S. Moon, S. J. Kenny, K. Xu, Spectrally resolved and functional super-resolution microscopy via ultrahigh-throughput single-molecule spectroscopy. *Acc. Chem. Res.* 51, 697–705 (2018).
54. M. Ovesný, P. Křížek, J. Borkovec, Z. Švindrych, G. M. Hagen, ThunderSTORM: A comprehensive ImageJ plug-in for PALM and STORM data analysis and super-resolution imaging. Bioinformatics 30, 2389–2390 (2014).

55. R. E. Thompson, D. R. Larson, W. W. Webb, Precise nanometer localization analysis for individual fluorescent probes. Biophys. J. 82, 2775–2783 (2002).

56. W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects. Phys. Rev. 140, 5048–5079 (1965).

57. G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B Condens. Matter Mater. Phys. 54, 11169–11186 (1996).

58. W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects. Phys. Rev. B Condens. Matter Mater. Phys. 54, 11169–11186 (1996).

59. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).

60. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

61. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

62. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

63. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

64. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

65. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

66. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 82, 2775–2783 (1999).

J.C. conceived the project and designed the experiment. A. Radenovic supervised and coordinated the project. J.C. performed the experiments and data analysis with help from E.G., M.Z., and A.A. A. Rayabharam performed DFT and AIMD simulations under the supervision of N.R.A. K.W. and T.T. contributed materials. J.C. wrote the manuscript with input from all authors.

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