

Supplementary Materials for

Anomalous interfacial dynamics of single proton charges in binary aqueous solutions

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Supplementary Information

Anomalous interfacial dynamics of single proton charges in binary aqueous solutions

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A] Experiments



Figure S1. Evolution of interfacial surface state and ensemble spectra in pure EtOH. Evolution of the ensemble spectra, right after solvent exchange (blue) and after one hour (red). The relative increase of the spectral population above 610 nm is consistent with the occurrence of a slow adsorption process at the flake's surface in the presence of pure organic solvent.



Figure S2. Normalized distribution of emitted photons per frames (20 ms integration time) for all defects (blue) and for defects which were attributed a spectra (red). The red distribution in skewed towards larger photon counts. Experimental conditions: $X_{H2O} = 0.4$ in water/acetone mixture.



Figure S3. hBN flake in contact with dodecane. (A) Variation of the total photoluminescence intensity emanating from the flake upon laser illumination, as a function of time. Upon illumination ("laser ON"), we evidence an initially large and homogeneous photoluminescence signal (B), which progressively decreases over time leading to discernable emitters and reaching a steady-state level in intensity and number of emitters (C). This bleaching is reversible and the large photoluminescence intensity is recovered upon sufficiently long dark time (several minutes).

The reversible bleaching evidenced in Fig. S3 allows us to propose the three-state model of Fig. 1C, where luminescence at $\lambda_{\rm B} \sim 630$ nm is attributed to the specific interaction (e.g. adsorption) of hydrophobic alkyl groups of the organic solvent (dodecane, methanol, ethanol or acetone) with defects as $D_2 + CH_3 - R \rightarrow D_2(CH_3 - R)$. Upon laser excitation, defects reach their excited state $D_2(CH_3 - R)^*$, upon which they can relax back to ground state by emitting a photon (Fig. 1C, red arrow) or desorb the alkyl groups $D_2(CH_3 - R)^* \rightarrow D_2 + CH_3 - R$. This three-state diagram can phenomenologically describe our observations. As shown in Fig. S4, this reversible bleaching upon illumination is also observed in the binary mixtures, as well as in pure water [26].



Figure S4. hBN flake in contact with a binary solution (water/ethanol) with $X_{H20} = 0.5$. Variation of the number of emitters per frame as a function of time upon laser illumination, showing a progressive decrease towards steady-state level over time.



Figure S5. Variation of surface state and interfacial diffusion coefficient for flakes in contact with water/EtOH and water/MeOH mixtures. (A-B) Normalized density ρ_i/ρ_i^0 of active defects of type A and B, (C) relative proportion of the spectral population θ_A and (D) variation of interfacial diffusion coefficient as a function of water volume fraction X_{H20} on two distinct flakes in contact with water/EtOH mixtures. (E) Comparison of the interfacial diffusion coefficient on the same flake, in two mixtures of water/MeOH and water/EtOH at 50% volume fraction.



Figure S6. Ensemble emission spectra of defects in dodecane (orange) and acetone (red). A 10 nm redshift from 635 nm to 645 nm is observed for increasing solvent polarity, consistent with an interaction between the dipole of the defect in its excited state and the solvent [49]. We have ϵ (dodecane) = 2 and ϵ (acetone) = 21.

B] Simulations

B.1 Defect adsorption and desorption barrier



Figure S7: Band structure. Band structure of V_B^- -hBN where defect state '1' is due to the boron vacancy.

Entropy effects

The adsorption and the desorption barriers calculated in Fig. 5B-C do not take entropy into consideration. In order to account for entropic effects, we calculate the entropic barriers using standard statistical mechanics. We calculate the entropic barriers for the reaction below, evaluating the change in translational, rotational and vibrational entropy between the products and the reactants.

$$H_3O^+ + V_B^{-1} \rightarrow V_BH + H_2O$$

We observe that the contribution to the free energy due to the entropic effects, $T\Delta S_{tot}$ is -0.508 eV. This value does not change with the molecules in the first coordination shell as the reactants and products do not change in the above reaction. This entropic contribution would have to be added to the desorption barrier and subtracted from the adsorption barrier. This effect thus leads to a net decrease of the free energy desorption barrier.

Note finally that the mixing entropy of the liquid itself is not considered in this entropic part. Calculations by Lama, et al. [52] show that methanol-water mixtures achieve a maximum mixing entropy value at 60% water concentration. This additional mixing entropy would additionally contribute to decrease the desorption barriers for these mixtures.

Entropy calculations

The entropies for the reactants and the products are calculated using the following statistical mechanics formulation [60]

$$S_{3D,trans} = k_B N. \ln\left(\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \cdot \frac{V}{N}\right) + \frac{5}{2} \cdot k_B N$$
$$S_{\text{vib},s} = k_B N. \left(\frac{\frac{\theta_{\text{vib},s}}{T}}{e^{\frac{\theta_{\text{vib},s}}{T}} - 1} - \ln\left(1 - e^{-\frac{\theta_{\text{vib},s}}{T}}\right)\right) \text{ where } \theta_{\text{vib},s} = \nu_s \cdot \frac{h}{k_B}$$

$$S_{\rm 3D,rot} = k_B N \left(\ln \left(\frac{\pi^{\frac{1}{2}}}{\sigma_{\rm x} \sigma_{\rm y} \sigma_{\rm z}} \sqrt{\frac{T^3}{\theta_{\rm x,rot} \theta_{\rm y,rot} \theta_{\rm z,rot}}} \right) + \frac{3}{2} \right) \text{ where } \theta_{\rm rot} = \frac{h^2}{8\pi^2 k_{\rm B} I_z}$$

The reaction used for evaluating the entropies is as follows: $H_3O^+ + V_B^{-1} \rightarrow V_BH + H_2O$

It is assumed that the translational, rotational and the vibrational entropies of the hBN surface do not change in the reaction, therefore the vibrational entropy of V_BH would be the only contributing factor for that. The individual components of entropy are calculated for H_3O^+ in the reactants and H_2O in the products to obtain

$$\Delta S_{\text{trans}} = -6.988 \times 10^{-6} \frac{eV}{K}$$
$$\Delta S_{\text{rot}} = -3.3622 \times 10^{-5} \frac{eV}{K}$$
$$\Delta S_{\text{vib}} = -1.653 \times 10^{-3} \frac{eV}{K}$$

The total entropic contribution to the barrier would therefore be $T\Delta S = -0.508 \ eV$

Excited state barrier calculations

Calculating the band structure of the hBN surface with a negatively charged boron vacancy, we observe that there is an additional band in between the conduction and the valence bands, which can be accessed by electrons once they are excited. The energy barrier between a proton and an excited V_B^- defect is calculated to quantitatively evaluate the effect of defect excitation on its reactivity. We observe a respective increase and decrease of the static adsorption and desorption barriers (table S1).

	2 water	1 MeOH, 1 water	2 MeOH
Ground state (eV)			
Adsorption	0.2406	0.2801	0.2948
Desorption	3.2289	3.1156	3.2022
Excited state (eV)			
Adsorption	0.2737	0.3999	0.3979
Desorption	2.6231	2.4108	2.4266

Table S1. Computed proton adsorption and desorption energy for different molecules in the first solvation shells of the hydronium ion and for defects respectively in the ground and excited state.

B.2 Mechanistic interpretation of the variation of the defect desorption energy with solvent content

The non-monotonic behavior of the desorption barrier reported in Fig. 5 and above could be due to a variation in the interfacial density profile, and in particular to a variation of the distance between the surface and the first layer of solvent molecules. As shown in Fig. S8, density profiles were calculated for 0%, 25%, 50% and 100% methanol-water mixtures. The location of the density peaks does not change with concentration of methanol, and thus does not contribute to the non-monotonic behavior of the desorption barrier



Figure S8. Interfacial density profile. (A-C) Snapshot of simulation box for **(A)** pure water, **(B)** 50% water and **(C)** 0% water. **(D-F)** Associated density profile with respect to the distance from the hBN sheet, decomposed into total density **(D)**, water density **(E)**, and MeOH density.



Figure S9. Difference in charge density of the solvating molecules between two solvation states. The following conditions are shown: (A) Charge density difference between 50% MeOH and 100% water. (B) Charge density difference between 100% MeOH and 100% water. (C) Charge density difference between 50% MeOH and 100% MeOH. The 2-water system in the first solvation shell is representative of the 100 % water system, the 1 MeOH-1 water is representative of the 50% MeOH and the 2 MeOH is representative of the 100% MeOH system. The systems are shown in a transient step during the desorption of H⁺ from $V_{\rm B}^-$. Blue indicates a positive charge density difference (increase in electrons). Yellow indicates a negative charge density difference (decrease in electrons).

To rationalize the observed variation of the desorption barrier with solvent content, we turn in Fig. S9 to the analysis of the charge density of the solvating molecules. We show in

Figs. S9A-B, the difference in charge density when methanol is present in the first solvation shell of the hydronium ion compared to the pure water case. As evidence in these plots, 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. This charge redistribution enhances the basicity of the aqueous core and leads to a decrease in the desorption barrier of H^+ . This effect is present in both the 50% and the 100% methanol system and is consistent with previous work [38]. In addition, this configuration also leads to an increased Coulombic attraction between the H^+ and the methanol electron cloud, which will contribute to the decrease in the desorption barrier of H^+ .

Comparing the case of 100% methanol (Fig. S9B) and 50% methanol (Fig. S9A), we see that the electron cloud of the methanol at (#) is similar in shape. However, at the location of the 2nd molecule in the solvation shell (*), the yellow electron cloud (representing a decrease in electron density) is closer to the hydronium ion, which would slightly increase the desorption barrier of the 100% methanol compared to the 50% methanol.

This effect can be seen more effectively in Fig. S9C. The MeOH molecule represented by (#) on the right is the same for both cases. Slight changes in the orientation of the molecule leads to the observed change in the charge density difference on (#). At (*), we evidence an increase in charge density (increase in electron density), which decreases the desorption barrier for 50% MeOH system, due to the decreased Coulombic attraction between the electron cloud at (*) and the H^+ ion.

B.3 Proton segregation at a pristine interface

As shown in Fig. S10, we indeed observe a physisorption well for the three conditions of 100% water, 50% water and 0% water, showing that the positively charged hydronium ions prefer to stay around 3-3.5 Å away from the surface. We observe in these simulations a decrease in the physisorption well from 0.28 to 0.05 eV as the concentration of methanol increases.



Fig. S10 : Free energy profiles (Potential of Mean Force, PMF) of 100% water, 50% methanol and 100% methanol with respect to the distance of the hydronium ion from the hBN surface.

C] Supplementary Movies

Supplementary Movie 1 Wide-field movie of defect activation dynamics at the flake's surface for water/acetone mixture, with $X_{H2O} = 0.6$.