

# Direct Measurement of Water-Assisted Ion Desorption and Solvation on Isolated Carbon Nanotubes

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Cite This: https://dx.doi.org/10.1021/acsnano.0c05638 **Read Online** ACCESS Metrics & More Article Recommendations s Supporting Information ABSTRACT: We have investigated the change in mean Ion surface Ion water residence time of gaseous ions adsorbed on the surface of layer hopping adsorption <del>მ</del>ენტზემენტზე suspended carbon nanotube field-effect transistors (CNT-FETs) Increased mean CNT

suspended carbon handoube held-effect transistors (CN1-FE1s) with and without native surface water layers that exists in atmospheric conditions. Devices were characterized electrically before and after dehydration by thermal, dry gas, and vacuum desiccation and in each scenario were found to have substantially higher mean ion residence times. It is proposed that water molecules native to the CNT surface in ambient conditions provide a reduction pathway for incoming gaseous ions, yielding hydronium ions  $(H_3O^+)$ . This is supported by the appearance of frequent clustered readsorption events in the presence of surface water, caused by the rapid hopping of H<sup>+</sup>



between the device surface and the lowest water layer, which are not present in data collected from desiccated devices. After desiccation of the device, a thermal trial was conducted to determine the adsorption energy of  $N_2^+$  ions on the CNT surface. This work has profound implications for our understanding of wetting in one-dimensional systems and the chemistry of ion chemisorption and solvation on the surfaces of materials in general.

**KEYWORDS:** carbon nanotubes, ionic surface interactions, interfacial water, carrier scattering, Grotthuss mechanism, molecular adsorption energy

s semiconductor device structures continue to scale toward the limit of one-dimensional channels, it is becoming increasingly necessary to investigate how surface dopant dynamics effect charge conduction in restricted environments. To that end, carbon nanotube field-effect transistors (CNT-FETs) act as an ideal experimental platform to further study these effects. The inherently 1D nature of the CNT-FET along with its great versatility through electrostatic gating makes it a highly sensitive probe for the detection of molecular/ionic interactions with the CNT surface. CNT devices have already been used successfully in the development of gas and biological sensors in recent years via their extremely high surface-to-volume ratio, which makes them electrically sensitive to surface adsorbates.<sup>1,2</sup> Devices that make use of single suspended CNTs especially have the capability of monitoring individual ionic interactions with device surfaces without the noise induced by substrate defects.<sup>3–10</sup>

In agreement with previous reports<sup>8–10</sup> we have found that, in the presence of positive gaseous ions generated by radiation exposure, suspended CNT-FET devices undergo large switching events in conduction characteristics. These events are attributed to the interaction of individual gaseous ions with the surface of the CNT conduction channel.<sup>10</sup> As ions approach the CNT surface, an electrostatic potential barrier forms in the valence band (Figure 1a), hindering charge carrier transport, thereby reducing the current, shifting the gate voltage threshold, and increasing the subthreshold swing of the device, which can be seen in the repeated back gate voltage sweeps depicted in Figure 1b. Unlike Coulomb scattering in 2D MOSFETs,<sup>11,12</sup> holes in the valence band have no unobstructed path to avoid the electrostatic barrier in the one-dimensional CNT channel. This results in the large (1–2 orders of magnitude) drop in the conduction of the devices, a far greater effect than the traditional gate screening induced by

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Figure 1. Ionic interaction with CNT device conduction: (a) Cartoon representation of ionic surface dopant on a CNT device channel with accompanying plot of the Coulomb potential barrier in the valence band along the length of the CNT. (b) Repeated gate voltage dependent transport samples of a device depicting both nominal p-type behavior (without the adsorbed ion species) and large reduced state sweeps (with the adsorbed ion species). (c) Exemplary data, collected at  $V_g = 0$ , depicting three large switching events in device conduction. The black box outlines the zoomed-in plot of the first switching event (d), which shows sharp transitions between the two conduction states of the device. The reduced CNT conduction state is a result of ion adsorption at the CNT surface, and thus its duration corresponds with the ion residence time on the surface.

substrate defect traps in traditional surface-supported CNT-FETs,<sup>13,14</sup> which occur further from the conduction pathway.

In an effort to further characterize these events, we have monitored device conduction at a fixed back gate voltage  $(V_g)$ , effectively monitoring a device at a vertical slice of Figure 1b  $(V_g = 0)$  as it evolves over time (Figure 1c). While doing this in the presence of gaseous ions, we observe the sharp transitions from nominal device conduction to a reduced conduction state caused by ionic adsorption. From these data we are then able to extract the individual ion residence times on the CNT surface by recording the duration of the reduced conduction state (Figure 1d).

In further experiments building on these previous results,<sup>8–10</sup> using meticulously controlled sample chamber, environmental conditions, and vastly expanded measurement dynamic range and duration, we have found that the durations of these large transient ion adsorption events are strongly affected by the existence of surface-adsorbed water. Atmospheric water has long been known to coat surfaces in ambient conditions<sup>15–20</sup> and often serves as a highly persistent contaminate of the internal surfaces of ultra-high-vacuum systems, where it is so tightly bound that high-vacuum baking or UV treatment is often required for its removal.<sup>21</sup> Though originally thought to be hydrophobic in nature, CNTs and graphene are no exception to this phenomena.<sup>22–27</sup> The existence of surface water and other liquid solvents has been extensively investigated in CNT and graphene device systems

and has been linked to changes in many device characteristics.<sup>26–34</sup> By measuring red-shifts in the photoluminescence spectrum of suspended CNT devices (like those detailed in our work) Homma *et al.*<sup>26</sup> showed that the presence of water layers on the CNT surface is sensitive to environmental water vapor pressure, undergoing what appears to be a first-order phase transition in surface coverage about a critical pressure. This finding is supported by MD and DFT simulations investigating the formation of water on graphene and CNT surfaces<sup>22–27</sup> that indicate multiple layers of self-assembled hydrogen bond networks up to 11.3 Å thick.<sup>26</sup>

The interplay between the dynamics of ion reduction/ solvation *via* water and the rate and lifetime of ion adsorption events on the surface of CNTs is particularly important to the development and understanding of future CNT device applications and for the understanding of ion–surface interactions in general. This work seeks to both better our understanding of reliability in nanoscale device structures for future low-power electronic applications and also display the efficacy of this system in identifying the individual adsorption energies of gaseous species at electrically tunable surfaces. This second assertion is key to bettering our fundamental understanding of ion-doped surfaces, with applications to the study of ion dynamics in mitigating or tuning electrostatic discharge (ESD) at charged surfaces,<sup>35,36</sup> surface modifications of various carbon-based and polymer substrates using corona discharge,<sup>37,38</sup> and directed cold atmospheric plasma treat-



Figure 2. Evolution of the mean ion residence time ( $\tau_{ion}$ ) over the course of the multiple experimental protocols: (a)  $\tau_{ion}$  versus temperature, with arrows showing the direction of temperature sweeps for the initial heating phase (orange), the cooling phase (blue), and secondary heating phase (purple). Data taken below 51 °C after the initial heating phase are permanently locked into the low conduction state (red) due to overlapping events. The plotted points in these cases represent the total experiment run time at these temperature set points. (b)  $\tau_{ion}$  at 25 °C plotted versus experiment stage, including data taken after a 3-day recovery period in atmospheric conditions. (c)  $\tau_{ion}$  evolution in 3 h intervals over the course of ~60 continuous hours of dry gas desiccation.



Figure 3. Exemplary data before and after vacuum desiccation. Time-dependent conduction data taken before (a) and after (b) vacuum desiccation showing a large increase in the reduced conduction state, corresponding to increased ion/surface residence.

ments, which are of growing importance as a therapeutic method in the medical community.<sup>39</sup> With measurements of these water/ion/CNT interaction events at the level of the individual adsorbed particle, this work is well positioned to increase this understanding.

## **RESULTS AND DISCUSSION**

Figure 2a shows the evolution of mean ion residence time  $(\tau_{ion})$  over the course of the thermal desiccation phases during which water was evaporated off the CNT surface. During heating phase 1 (orange), the device was heated from 25 °C through preset temperature set points (25, 37, 51, 63, and 71

°C). Source current sampling data were collected in dry N<sub>2</sub> at each temperature for approximately 7 h, with 25 710 switching events measured. Accompanying the increase in temperature is a decreasing trend in  $\tau_{\rm ion}$ . After the initial heating phase, the temperature points were retraced cooling the device to room temperature (blue). During this phase,  $\tau_{\rm ion}$  shows a drastic increase at all temperatures, showing the sensitivity of ion residence to the presence of adsorbed water on the device. Finally, the device was reheated (purple) and  $\tau_{\rm ion}$  again decreased with increasing temperature, while values at each temperature step increase slightly further but remain consistent with the newly dehydrated state. After heating phase 1, for

measurements at 25 and 37 °C the source current remained locked into the low conduction state throughout the entire 7 h measurement time. The residence times reported in Figure 2a at these temperatures correspond to this duration, where the  $\tau_{\rm ion}$  has increased to the point of consistently overlapping events. Figure 2b plots  $\tau_{\rm ion}$  at 25 °C during experimental stages, and after 3 days of atmospheric exposure, showing a nearly complete recovery of the original (shorter)  $\tau_{\rm ion}$ .

An alternative method utilized to remove water from the CNT surface was desiccation in a dry gas environment. Here data were collected continuously for approximately 60 h in a constant flow of dry N<sub>2</sub>. Data containing over 16 000 switching events were then separated into segments of approximately 3 h in length and analyzed to determine the evolution of the  $\tau_{ion}$  over the course of the experiment. This analysis is summarized in Figure 2c showing a steady increase in  $\tau_{ion}$  as a function of desiccation time.

Finally, we compare data collected before and after vacuum desiccation. The device was held in a vacuum for 1 h at 22 °C, which has been previously shown to be an effective method for water removal.<sup>26</sup> The effect of desiccation on individual ionic residence can be seen in the data shown in Figure 3a and b, where we note the drastic increase in all but one ionic residence. Analysis of approximately 294 min of data with 728 measured events leads to a rise in  $\tau_{\rm ion}$  from ~270 ± 92 ms initially to ~774 ± 117 ms after desiccation.

Previous work by Bushmaker *et al.*<sup>10</sup> analyzed data taken from repeated 40 s sampling periods of device conduction in the presence of a Co-60 source in a dry gas environment. Each 40 s sampling trail was immediately followed by approximately 10 s of "dead time", where the device was held at ground while the data measured in the preceding trail were saved to file. These repeated samples possessed both high resolution and a low noise floor, which allowed for the detection of consistent multilevel behavior in the low conduction state signal. These multiple signal levels corresponded to quantized increases in device resistance and were thus attributed to multiple ions concurrently adsorbed to the CNT surface, which appear to act completely independently. Analysis of the event frequency as a function of the number of interacting ions was well fit to the expected Poisson distribution for noninteracting events. Thus, ions adsorbed on the surface of a device can be thought of as series resistors, where each subsequent drop in device conduction (rise in resistance) is attributed to the addition of a single ion to the system. In this study, we focus on the collection and characterization of the exact durations of each ionic interaction. Given this, we adjusted our experimental setup, such that it would be capable of continuously measuring the device. This is very important in the case of dehydrated devices where the event duration becomes larger, that is, on order of or even exceeding the 40 s sampling limit of previous trials. In these cases, any events that fell within the "dead time" or on the boundaries of the sampling trial (starting before or ending after each sample) would be lost due to our inability to accurately determine the event duration. By continuously measuring the device throughout the entire experiment we can accurately determine event start and end times, without risk of them falling partially or entirely between separate sampling trials.

The caveat to this transition is that the experimental setup did not possess the low current resolution to resolve multipleion events. This can lead to a discrepancy between the measured duration of a switching event and the actual ionic residence time in high duty cycle data, where ion arrival rates are high relative to residence times, causing some individual events to overlap. For ion adsorption duty cycles higher than  $\sim 2\%$ , the probability of overlapping events becomes significant, resulting in an overestimation of ion residence based purely on the amount of time spent in the low current state. Given the broad range and evolution of individual residence times measured over the course of the experiments, it is difficult to set the ion arrival rate to avoid event overlap over the entirety of a multiday experiment while also encouraging enough events to collect meaningful statistics. To address this, we performed a Monte Carlo simulation over a large range of simulated data set sizes, measured duty cycles, and expected residence times to determine an ion residence duration correction factor ( $CF_{duration}$ ). This correction factor converts the measured mean switching event duration, which could be inflated as a function of multiple ionic interactions at high duty cycles, into the mean ion residence time  $( au_{ion})$  for individual ion adsorption. We found this factor to be

$$CF_{duration} = \frac{\lambda}{e^{\lambda} - 1}$$
(1)

where  $\lambda$  is the standard Poisson parameter and duty cycle = 1 -  $e^{-\lambda}$ . Greater detail of this simulation along with figures pertaining to its validity under various conditions can be found in the Supporting Information (S2–S5). Results presented for  $\tau_{\rm ion}$  that were obtained at duty cycles higher than 2% have been corrected with the above factor. The average number of ions on the CNT at a given time can be calculated from the Poisson distribution. For reference, the data shown in Figure 2a had duty cycles ranging from a low of 0.0975%, corresponding to an average number of ions on the CNT of 0.000 98 ions, to a high of 76.8% (excluding locked-down measurements), corresponding to an average number of ions on the CNT of 1.46 ions, with a corresponding correction factor CF<sub>duration</sub> = 0.441.

To understand the effect of thermal desiccation on the ion residence, we must first consider how the mean ion residence time is expected to change as a function of surface temperature. The standard treatment for adsorption kinetics of noninteracting particles at solid surfaces describes the mean residence time of an adsorbed ion to be

$$\tau_{\rm ion} = \tau_0 e^{\left(-E_a/k_{\rm b}T\right)} \tag{2}$$

where  $E_{\rm a}$  is the particle/surface activation energy of adsorption (referred to as the adsorption energy hereafter) and  $\tau_0$  is related to the period of oscillation of the surface.<sup>15–17</sup> Thus, with increasing temperature of the system one should expect a drop in the residence time of adsorbed species.

This inverse relationship between residence and temperature is consistent with each phase of the experiment presented in Figure 2a, except for the data collected in heating phase 1 at 71 °C, where we see a small rise  $\tau_{ion}$ . We credit this anomalous data point to the simultaneous desiccation of the device due to prolonged heating and exposure to dry N<sub>2</sub> during heating phase 1. Here, the desiccation effect overcomes the temperature dependence of desorption, resulting in a minor increase in residence time. While most noticeable at this final data point, this desiccation effect is present at every point of the first heating phase, and it is this convolution of temperature effects with the desiccation that makes fitting this data to eq 2 impossible. In a device without this competition between



Figure 4. Mean residence time of adsorbed species on CNT surfaces: Plots of eq 2 with respect to temperature (a) and adsorption energy (b) where  $\tau_0 = 100 \text{ cm}^{-1}$ , the radial breathing mode of the CNT. Both plots display the very large range of expected mean adsorption times that are highly sensitive to surface adsorption energy. These range from nanoseconds for weakly physiosorbed particles (0.2 eV) to many days for chemisorbed particles (1.0 eV).

temperature and desiccation, one should expect the subsequent thermal cycling to retrace the same curve along a plot relating  $\tau_{\rm ion}$  to the system temperature. Instead, our data show the large influence of adsorbed water when comparing the data taken at fixed temperatures after thermally cycling the device. As described earlier, Figure 2a shows that the result of the first heating phase leads to a drastic increase in  $\tau_{ion}$  at all temperatures displaying the direct result of dehydrating the tube on the mean residence of adsorbed ions. The further small increase in  $au_{\mathrm{ion}}$  after the second heating phase is attributed to the further desiccation of the device surface by extended periods in a dry N2 environment at elevated temperature. This behavior was reproduced in tests on greater than 10 separate devices, without exception. Experiments were also repeated in the same device after re-exposure to atmospheric conditions for several days (Figure 2b). Here the device recovers its normal behavior at room temperature, with shorter ion-adsorption lifetimes when exposed to ionized gases. The device can then be reheated and again exhibits longer ion-adsorption lifetimes. The increase of the mean ion residence and the recovery of devices when re-exposed to atmospheric conditions are common features throughout all three experimental procedures.

In the data of Figure 2a there is not only a convolution of temperature and desiccation alone but also the competition between two desiccation mechanisms, that of applied heat and dry gas exposure. During heating cycles this is unavoidable since the flow of dry gas acts as the source of ionizable particles with which switching events are generated. We are however able to monitor the effect of dry gas desiccation directly on a pristine device at room temperature as depicted in Figure 2c. Here the desiccation is seen more gradually where water removal is expected to be slower due to the room-temperature, atmospheric-pressure conditions. This effect does not appear to saturate even after 60 h of gas desiccation. Thus, we show the ion residence time increase depends greatly on the desiccation technique, with heated desiccation resulting in larger changes than room temperature gas or vacuum desiccation.

We observe a correlation between the desiccation time and the time required to return to nominal behavior. This feature could be due to incomplete water desorption from the metal contact pads, where it is more tightly bound than the CNT surface, due to hydrophilic polar oxygen and hydroxyl terminations of the metal surface. Water on the metal contacts could act as anchor points on either side of the suspended CNT for the assembly of water networks across the tube surface. Still present after shorter desiccation exposures, these anchors could allow for faster rewetting of the CNT upon exposure to atmosphere. Even still, gas desiccation trials lasting just 24 h at room temperature required more than 40 h in ambient conditions for full device recovery.

We note that one could consider the ionization or removal of some other surface contaminate, like O2 or organic polymers, as potential contributors to the presented data. We believe this to be unlikely given the expected adsorption/ desorption kinetics for those species. Considering the case of O<sub>2</sub> or other atmospheric contaminates, it is theorized that such molecules would have very weak surface adsorption energies<sup>40,41</sup> Given the extremely short expected residence time for such weakly bound contaminates (Figure 4), one would also expect them to desorb quickly from the surface (on the order of fractions of a second in conservative estimations). Once the device is transferred to a pure dry N<sub>2</sub> gas environment, there is no way for the desorbed contaminates to be replenished, and thus their effect would drop much faster than that which we see in our data, which is observed to be continually evolving over many hours in each experimental protocol. In the case of bound organics, we first bring attention to the method of device fabrication, which is done via chemical vapor deposition (CVD) and without any postprocessing after CNT growth. This method removes major sources of contamination that are found using alternative methods such as drop casting ligand-supported CNTs and/or lithographic resist residues that are unavoidable when defining device structures after CNT growth. We do acknowledge that migration of contaminates onto device surfaces has been shown by storage in polymer carrying containers.<sup>42</sup> While these contaminates could reside on the device surface, these molecules are known to have very high adsorption energies.<sup>43</sup> Thus, in contrast to the weakly bound atmospheric contaminates, the removal of these polymers by gas desiccation would take many days (Figure 4).

These results demonstrate that native water layers play an important role in the dynamics of particle—surface interactions at the smallest scales. Our data suggest an interaction between water molecules and the incoming gaseous ion species that act as a relaxation mechanism for ionic adsorption at the CNT



Figure 5. Rapid readsorption events due to ion hopping between the CNT surface and lowest lying water layer. (a) Exemplary data depicting clustered switching events due to frequent reabsorption events near the CNT surface. Data can be broken into three distinct stages depicted in (b). Stage 1: the device is functioning nominally in a high conduction state with either no ion present in the system or the ion totally screened by large amounts of surface adsorbed water. Stage 2: an  $N_2^+$  has landed on the device and been reduced by the surface adsorbed water, and the resulting  $H_3O^+$  or  $H^+$  has adsorbed on the CNT surface. This shunts the device conduction, leaving it in a low conduction state. Stage 3: frequent switching events caused by rapid  $H^+$  hopping between the CNT surface and lower lying water layers resulting in the partial recovery of the device.



Figure 6. Comparison of event frequency with and without adsorbed water. Clustered switching events histograms depicting the time between adsorption events (TBE) on a logarithmic scale for events with (a) and without (b) adsorbed water, removed by vacuum desiccation. The presence of the unexpected peak at lower time bins is evidence of rapid ion desorption and readsorption between the CNT surface and adsorbed water layers that is not present after vacuum desiccation. When fit by  $r_{ion}$ , as calculated from the data mean and median TBE, we find poor agreement in the predesiccated device due to a large shift toward shortened times caused by rapid ion readsorption.

surface, resulting in shorter ion residences. Recent work by T. Inaba and Y. Homma<sup>28</sup> details the shift and degradation of photoluminescence from CNT devices (similar to those in this work) when exposed to atmospheric ions in air. This observation is attributed to the chemisorption of hydronium molecules  $(H_3O^+)$  on the CNT shifting the local dielectric function near the device surface. Similarly, our results are well described by the generation of hydronium ions within the adsorbed water layers by the reduction of the incoming flux of  $N_2^+$  ions. In the presence of humidity, atmospheric ions ( $N_2^+$ ,  $O_2^+$ ) are effectively reduced, transferring charge from atmospheric water, generating hydronium molecules as a byproduct.<sup>44–47</sup> It is highly likely that this happens as  $N_2^+$  and  $O_2^+$  ions interact with the surface water layers on CNTs. In aqueous environments, hydronium ions become solvated by the surrounding water molecules,  $^{48-50}$  resulting in the formation of hydronium core water clusters of the form  $(H_3O^+)[H_2O]_n$ . This hydronium, or the spare proton associated with it, is highly mobile in solution via a combination of thermal diffusion and proton hopping along adjacent water molecules known as the Grotthuss mechanism.<sup>51,52</sup> In this framework, our results prior to the removal of the water from the device show the interaction of the CNT device with either the hydronium ion itself or with a free H<sup>+</sup> transferring directly to the CNT surface. Evidence for these processes has been presented in MD simulations on graphene and other hydrophobic surfaces.<sup>53–57</sup> We note specifically two studies. First is simulations by Cole *et al.*,<sup>57</sup> which show that, when distributed in an electrolytic solution over a graphene sheet, H<sub>3</sub>O<sup>+</sup> ions are found preferentially near the graphene/ water interface at a separation distance equal to the height of the first water layer. Second, simulations of single hydronium ions over graphene surfaces by Mohammadi *et al.*,<sup>53</sup> show direct proton transfer back and forth between the carbon lattice and an adjacent water molecule.

Evidence for interaction between ions and the adsorbed water layers was found by further analyzing a shift in event frequency as a function of device desiccation. The presence of a host water layer, in which solvated ions/hydronium can reside between switching events, leads to desorption/readsorption events at a rate independent of, and much higher than, the gas-phase ion arrival time. We observe this feature in the form of frequent clustered switching events, an example of which is shown in Figure 5 along with an illustration of the ion positions resulting in the device conduction states.

Without the complication of any water interaction in the system one expects the arrival of incoming ions to follow a standard Poisson process.<sup>15–17</sup> Here, the expected time between detectable events (TBE) follows an exponential distribution  $e^{-tr_{ion}}$ , where  $r_{ion}$  is the rate of incoming ions (in counts per second, cps) and is calculated directly from the data as  $r_{ion} = 1/mean(TBE)$ . Histograms showing the distribution of times between observed events for those collected before and after the vacuum desiccation of a CNT device are plotted in Figure 6. Comparing these plots, we note the anomalous peak in the shortest time bin in the presence of water (Figure 6a), well above the exponential trend of the remaining data. A fit of the predesiccation distribution to  $r_{ion} = 0.0465$  cps, as calculated from the mean of the data, shows a poor fit that underestimates shorter time bins, while sloping too sharply for the remaining data. This stems from the shift toward smaller times by rapid readsorption mentioned above and can be better visualized by considering the relationship between  $r_{ion}$ and the median time for an exponential distribution  $(r_{ion} =$ LN(2)/(median(TBE)). This drastically higher  $r_{ion}$ , stemming from a small median value, fits the first two bins quite well, but slopes far too quickly for larger times. For a true exponential distribution, the value of  $r_{ion}$  should be the same, regardless of the mean or median derivation. This is the case for the postdesiccation histogram, where the mean and median values differ by only 0.000 12, which produces indistinguishable fit lines, where the mean  $r_{ion} = 0.0382$  cps is shown in Figure 6b. We propose that the peak in the predesiccation data arises from the multiple rapid ion readsorptions (Figure 5) as they switch between the tube surface and the lowest water layer, where they are partially screened and no longer follow the Poisson rate constant dictated by the source, but are instead much quicker, thereby shifting the mean and median values toward lower times (higher  $r_{ion}$ ). Fitting this data without the anomalous peak produces a good fit to an exponential distribution (Figure 6a, black) and predicts an  $r_{ion} = 0.0249$ cps, which is in agreement with the postdesiccation results. In contrast, after water removal (Figure 6b) we find good agreement with the expected distribution for all data as  $N_2^+$ ions adsorb and desorb with no interference due to the water lavers.

It is possible that the observed adsorption/desorption events are a mix of many dynamic interactions at the surface, including direct ion adsorption, hydronium adsorption, and direct proton transfer, which are greatly affected by the lower lying adsorbed water layers. Ions in the presence of water near the surface not only feel the adsorption interaction of the surface itself but also the solvation potential of the available water, which lowers its effective activation energy. As the system is slowly desiccated (by either heat or dry gas), there becomes less water available to solvate the surface ion, leading to a steady increase in  $au_{
m ion}$  during desiccation. We hope to gain a deeper understanding of this phenomenon in further experiments by systematically varying the system humidity, device gate bias, and surface-adsorbed species. One could also consider an in situ measurement with concurrent Raman measurement of the CNT radial breathing mode (RBM). The RBM has already been shown to be sensitive to surface adsorbates in a known manner  $^{26}$  and could be used to get a direct measure of the surface coverage in real time. We will also look to apply a dynamically changing incoming ion current to

account for the increased residence of the dehydrated CNTs and avoid event overlapping.

With the knowledge that desiccation of the device surface is required in order to capture the N<sub>2</sub><sup>+</sup> ionic interactions, another heated trial was conducted on a separate device after ~16 h of vacuum desiccation at 30 °C followed by a slow heating phase from 30 to 42 °C over the course of 3 days. Data were then collected from 44 to 56 °C, where the change in  $\tau_{\rm ion}$  is noticeable, but not so large as to risk overlapping events. Figure 7 presents  $\tau_{\rm ion}$  determined for each temperature set



Figure 7. Adsorption energy determination. Fit of heated trial after vacuum desiccation resulting in an adsorption energy between 756 and 781 meV for  $N_2^+$  ions on the CNT surface. In each fit the value of  $\tau_0$  was selected to correspond with upper and lower bounds of the CNT radial breathing mode. As a result, the adsorption energy of the ion is the only free parameter.

point along with a fit to eq 2, where the adsorption energy was determined to be between 756 and 781 meV depending on the selection of  $\tau_0$ , which is consistent with chemisorption on the CNT surface, significantly higher strength than that of a neutral N<sub>2</sub>.<sup>41</sup> Here,  $\tau_0$  of eq 2 was chosen in correspondence with the out-of-plane oscillations of the CNT surface, which are expressed by the radial breathing mode. The bounds for this value were selected to be 100 or 250 cm<sup>-1</sup>, in agreement with other studies of single-walled CNTs.<sup>27</sup> With this parameter fixed to each bound in Figure 7, the adsorption energy is the only free fitting parameter.

#### **CONCLUSIONS**

In conclusion, we have measured the mean residence time of gaseous ions on the surfaces of CNT devices before, during, and after thermal, gas, and vacuum desiccation. In all cases, dehydration of the CNT surface led to an increase in the mean residence time when compared to devices in ambient conditions, with thermally assisted desiccation resulting in increases of several orders of magnitude. Ion residence times are measured from large switching events induced by the electrostatic potential of the ionic species near the restricted conduction channel of the CNT. This shift in the ion residence time is attributed to adsorbed water layers, which, when present, cause solvation-assisted desorption of the ion from the CNT surface and reduce the incoming  $N_2^+$  ions, generating hydronium ions  $(H_3O^+)$ , whose spare proton is free to travel through the surface water layers. This claim is supported by the appearance of frequent clustered events, whose switching rate greatly exceeds that defined by the system and which disappear after device desiccation. After thorough desiccation of a device

surface, ionic events were monitored during a heated trial, and a fit of the adsorption energy of  $N_2^+$  on the CNT surface was determined to be between 756 and 781 meV. These results illustrate the capability of this system for studying a multitude of ion/liquid chemical reactions and adsorbed ionic defects at surfaces in the single dopant regime for varying device and environmental conditions, which is of growing importance as electronic device design, and applications continue to scale toward smaller dimensions.

## **METHODS/EXPERIMENTAL**

CNT-FETs are grown *via* CVD on prepatterned single-gate device architectures fabricated at the UCSB Nanofabrication Facility. The contact pattern consists of a 500 nm deep trench etched in a Si/SiO<sub>2</sub>/ Si<sub>3</sub>N<sub>4</sub> substrate. Lithographically defined Pt electrodes are then deposited on either side, and the bottom of the trench is deposited by electron beam physical vapor deposition (EBPVD) to function as source/drain and gate electrodes, respectively. Exposure windows are defined in a layer of photoresist to protect the electrodes and allow the selective deposition of the ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>) CVD growth catalyst. The finished wafer is cut into an approximately 0.5 cm square die containing 30 devices. The CVD process is tuned to achieve the suspension of a single, isolated CNT between the source and drain contacts, bridging the trench. This process yields extremely pure devices without extraneous defects generated by postprocessing or noise stemming from substrate interactions.<sup>3-11</sup>

As summarized in Figure S1 (see Supporting Information), temperature-dependent sampling measurements were undertaken in a custom ion drift gas chamber. Here, wire-bonded CNT-FET chip packages are secured by a customized chip carrier socket. The back side of the chip package is pressed against a copper thermal chuck/ heat pipe by way of clamps integrated into the electrical socket. The temperature of the device is measured by a surface-mounted resistance temperature detector (RTD) and is adjusted via a PIDcontrolled thermoelectric hot/cold plate (Newport 3040 TEC), which makes good thermal contact with the copper chuck. Electrical connections from the chip package and socket are routed in a layered printed circuit breakout-board to SMB sockets. The printed circuit board served a dual purpose as an airtight wall of the sample chamber, which held vacuum to <1 mTorr (gauge-limited measurement). The chamber is sealed on the back side with a custom KF flange that supports a small electrode upon which a 100 uCi 90Sr radioactive source is mounted. High-energy beta decay electrons from this source are used to ionize the volume of gas inside the chamber. Positive gaseous ions are then driven toward the device mount by a voltage applied to the flange-mounted electrode, in a drift chamber setup. The distance from the emitting face of the <sup>90</sup>Sr source to the CNT sample was approximately 7.4 mm. Drift chamber ion current versus electrode plate voltage for the 90Sr source shows saturation (majority of generated ions swept out of chamber before recombination) at around 4 V.

Several experimental protocols were followed in this work. In a thermal desiccation experiment the temperature of the sample mount was increased in an initial heating phase to 71 °C while the sample was in a dry N<sub>2</sub> gas purge. The sample was then cooled back to room temperature, and then the temperature was increased again. In a gas desiccation trial, the sample was exposed to dry N<sub>2</sub> at room temperature for long periods of time, thereby drying the CNT surface. Finally, the sample was exposed to vacuum for 1 h, at room temperate. In each case, switching events in device conduction were measured over the course of the experiment and compared with data collected in ambient conditions.

For all experiments the devices were operated near the subthreshold regime by applying a 100 mV source–drain bias  $(V_{sd})$  while holding the gate electrode at ground  $(V_g)$ . Source–drain current was then recorded in the presence of gaseous ions. During thermal desiccation this was done using an Agilent 4156C semiconductor parameter analyzer with a sampling frequency of 250 Hz in 40 s

intervals. For the gas and vacuum desiccation trials the biases were held constant and data were recorded continuously *via* a Tektronix DPO 3034 oscilloscope with a sampling frequency of 5000 Hz. Both pieces of equipment were integrated into a Labview VI, which allows for programmable and fully automated data collection. After collection, data were analyzed *via* a Python script to identify the time and duration of each large switching event.

The dry nitrogen gas used in this experiment was harvested by the evaporation of ultra-high-purity (UHP, 99.999%) liquid nitrogen  $(LN_2)$  stored on-site. Thus, we consider the lower bound on the evaporated nitrogen to be at the UHP level.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c05638.

Details of the Monte Carlo calculation; figures of the experimental design and the results of the Monte Carlo simulation (PDF)

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#### **Author Contributions**

P.J.E., B.W., and S.B.C. fabricated CNT FET samples. P.J.E. and A.W.B. designed the study, procured the experimental hardware, and collected and analyzed the data. A.W.B. performed Monte Carlo analysis. P.J.E. and A.W.B. wrote the paper. All authors commented on the manuscript.

# Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. Nanotube Molecular Wires as Chemical Sensors. *Science* **2000**, *287*, 622–625.

(2) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes. *Science* **2000**, *287*, 1801–1804.

(3) Bushmaker, A. W.; Deshpande, V. V.; Bockrath, M. W.; Cronin, S. B. Direct Observation of Mode Selective Electron-Phonon Coupling in Suspended Carbon Nanotubes. *Nano Lett.* **2007**, *7*, 3618–3622.

(4) Deshpande, V. V.; Bockrath, M. The One-Dimensional Wigner Crystal in Carbon Nanotubes. *Nat. Phys.* **2008**, *4*, 314–318.

(5) Deshpande, V. V.; Chandra, B.; Caldwell, R.; Novikov, D. S.; Hone, J.; Bockrath, M. Mott Insulating State in Ultraclean Carbon Nanotubes. *Science* **2009**, *323*, 106–110.

(6) Bushmaker, A. W.; Deshpande, V. V.; Hsieh, S.; Boekrath, M. W.; Cronin, S. B. Direct Observation of Born - Oppenheimer Approximation Breakdown in Carbon Nanotubes. *Nano Lett.* **2009**, *9*, 607–611.

(7) Sharf, T.; Kevek, J. W.; Deborde, T.; Wardini, J. L.; Minot, E. D. Origins of Charge Noise in Carbon Nanotube Field-Effect Transistor Biosensors. *Nano Lett.* **2012**, *12*, 6380–6384.

(8) Bushmaker, A. W.; Walker, D.; Mann, C. J.; Oklejas, V.; Hopkins, A. R.; Amer, M. R.; Cronin, S. B. Single Event Effects in Carbon Nanotube-Based Field Effect Transistors under Energetic Particle Radiation. *IEEE Trans. Nucl. Sci.* **2014**, *61*, 2839–2846.

(9) Bushmaker, A. W.; Oklejas, V.; Walker, D.; Hopkins, A. R.; Chen, J.; Cronin, S. B. Radiation Induced Single Ion Surface Effects in Nanoelectronic Circuits. *IEEE Trans. Nucl. Sci.* **2015**, *62*, 2926–2932.

(10) Bushmaker, A. W.; Oklejas, V.; Walker, D.; Hopkins, A. R.; Chen, J.; Cronin, S. B. Single-Ion Adsorption and Switching in Carbon Nanotubes. *Nat. Commun.* **2016**, *7*, 1–8.

(11) Ralls, K. S.; Skocpol, W. J.; Jackel, L. D.; Howard, R. E.; Fetter, L. A.; Epworth, R. W.; Tennant, D. M. Discrete Resistance Switching in Submicrometer Silicon Inversion Layers: Individual Interface Traps and Low-Frequency (1/f?) Noise. *Phys. Rev. Lett.* **1984**, *52*, 228–231.

(12) Kirton, M. J.; Uren, M. J.; Collins, S.; Schulz, M.; Karmann, A.; Scheffer, K. Individual Defects at the Si:SiO 2 Interface. *Semicond. Sci. Technol.* **1989**, *4*, 1116–1126.

(13) Liu, F.; Wang, K. L.; Li, C.; Zhou, C. Study of Random Telegraph Signals in Single-Walled Carbon Nanotube Field Effect Transistors. *IEEE Trans. Nanotechnol.* **2006**, *5*, 441–445.

(14) Wang, N. P.; Heinze, S.; Tersoff, J. Random-Telegraph-Signal Noise and Device Variability in Ballistic Nanotube Transistors. *Nano Lett.* **2007**, *7*, 910–913.

(15) De Boer, J. H. The Dynamical Character of Adsorption, 2nd ed.; Clarendon Press: Oxford, 1968.

(16) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Inerscience: New York, 1997.

(17) Israelachvili, J. N. Intermolecular and Surface Forces, 3rd ed.; Academic Press: Burlington, MA, 2011.

(18) Razouk, R. I.; Salem, A. S. The Adsorption of Water Vapor on Glass Surfaces. J. Phys. Colloid Chem. 1948, 52, 1208–1227.

(19) Hu, J.; Xiao, X.-D.; Ogletree, D. F.; Salmeron, M. Imaging the Condensation and Evaporation of Molecularly Thin Films of Water with Nanometer Resolution. *Science* **1995**, *268*, 267–269.

(20) Hamada, I.; Lee, K.; Morikawa, Y. Interaction of Water with a Metal Surface: Importance of van der Waals Forces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 115452.

(21) Danielson, P. Desorbing Water in Vacuum Systems: Bakeout or UV? R&D Mag 2001, 43, 57–59.

(22) Ma, J.; Michaelides, A.; Alfè, D.; Schimka, L.; Kresse, G.; Wang, E. Adsorption and Diffusion of Water on Graphene from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 033402.

(23) Iwasaki, D.; Suzuki, Y.; Watanabe, K. First-Principles Study of the Dielectric Functions of Carbon Nanotubes with Adsorbed Water. *Appl. Phys. Express* **2017**, *10*, 045101. (24) Akaishi, A.; Yonemaru, T.; Nakamura, J. Formation of Water Layers on Graphene Surfaces. *ACS Omega* **2017**, *2*, 2184–2190.

(25) Maekawa, Y.; Sasaoka, K.; Yamamoto, T. Structure of Water Clusters on Graphene: A Classical Molecular Dynamics Approach. *Jpn. J. Appl. Phys.* **2018**, *57*, 035102.

(26) Homma, Y.; Chiashi, S.; Yamamoto, T.; Kono, K.; Matsumoto, D.; Shitaba, J.; Sato, S. Photoluminescence Measurements and Molecular Dynamics Simulations of Water Adsorption on the Hydrophobic Surface of a Carbon Nanotube in Water Vapor. *Phys. Rev. Lett.* **2013**, *110*, 157402.

(27) Chiashi, S.; Kono, K.; Matsumoto, D.; Shitaba, J.; Homma, N.; Beniya, A.; Yamamoto, T.; Homma, Y. Adsorption Effects on Radial Breathing Mode of Single-Walled Carbon Nanotubes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 155415.

(28) Inaba, T.; Homma, Y. Atmospheric Ions as the Origin of Photoinduced Degrading of Photoluminescence from a Single-Walled Carbon Nanotube. *Appl. Phys. Lett.* **2015**, *107*, 071907.

(29) Kim, W.; Javey, A.; Vermesh, O.; Wang, Q.; Li, Y.; Dai, H. Hysteresis Caused by Water Molecules in Carbon Nanotube Field-Effect Transistors. *Nano Lett.* **2003**, *3*, 193–198.

(30) Na, P. S.; Kim, H.; So, H.-M.; Kong, K.-J.; Chang, H.; Ryu, B. H.; Choi, Y.; Lee, J.-O.; Kim, B.-K.; Kim, J.-J.; Kim, J. Investigation of the Humidity Effect on the Electrical Properties of Single-Walled Carbon Nanotube Transistors. *Appl. Phys. Lett.* **2005**, *87*, 093101.

(31) Bradley, K.; Gabriel, J. C. P.; Briman, M.; Star, A.; Grüner, G. Charge Transfer from Ammonia Physisorbed on Nanotubes. *Phys. Rev. Lett.* **2003**, *91*, 218301.

(32) Levesque, P. L.; Sabri, S. S.; Aguirre, C. M.; Guillemette, J.; Siaj, M.; Desjardins, P.; Szkopek, T.; Martel, R. Probing Charge Transfer at Surfaces Using Graphene Transistors. *Nano Lett.* **2011**, *11*, 132–137.

(33) Zahab, A.; Spina, L.; Poncharal, P.; Marlière, C. Water-Vapor Effect on the Electrical Conductivity of a Single-Walled Carbon Nanotube Mat. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2000, 62, 10000-10003.

(34) Inoue, S.; Tomita, Y.; Kokabu, T.; Matsumura, Y. Principles of Detection Mechanism for Adsorbed Gases Using Carbon Nanotube Nanomat. *Chem. Phys. Lett.* **2018**, 709, 77–81.

(35) Oda, T.; Ito, Y. Studies on Electrostatic Surface Discharges on Corona-Charged Polymer Surfaces. *IEEE Trans. Ind. Appl.* **1990**, *26*, 656–661.

(36) McCarty, L. S.; Winkleman, A.; Whitesides, G. M. Ionic Electrets: Electrostatic Charging of Surfaces by Transferring Mobile Ions upon Contact. J. Am. Chem. Soc. 2007, 129, 4075–4088.

(37) Leclercq, B.; Sotton, M.; Baszkin, A.; Ter-Minassian-Saraga, L. Surface Modification of Corona Treated Poly(Ethylene Terephthalate) Film: Adsorption and Wettability Studies. *Polymer* **1977**, *18*, 675–680.

(38) Zaldivar, R. J.; Nokes, J.; Steckel, G. L.; Kim, H. I.; Morgan, B. A. The Effect of Atmospheric Plasma Treatment on the Chemistry, Morphology and Resultant Bonding Behavior of a Pan-Based Carbon Fiber-Reinforced Epoxy Composite. *J. Compos. Mater.* **2010**, *44*, 137–156.

(39) Weltmann, K.-D.; von Woedtke, T. Plasma Medicine—Current State of Research and Medical Application. *Plasma Phys. Controlled Fusion* **2017**, *59*, 014031.

(40) Ulbricht, H.; Moos, G.; Hertel, T. Physisorption of Molecular Oxygen on Single-Wall Carbon Nanotube Bundles and Graphite. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2002**, *66*, 075404.

(41) Zhao, J.; Buldum, A.; Han, J.; Lu, J. P. Gas Molecule Adsorption in Carbon Nanotubes and Nanotube Bundles. *Nanotechnology* **2002**, *13*, 195–200.

(42) Reich, D. F. Sample Handling. In *ToF-SIMS: Surface Analysis by Mass Spectrometry*; Vickerman, J. C., Briggs, D., Eds.; IM Publications and Surface Spectra Limited, 2001.

(43) Godo, M.; Takatsuka, T.; Tomonari, M.; Miura, K.; Takami, S.; Kubo, M.; Miyamoto, A. Adsorption Behavior of Chemical Contaminants by Molecular Simulation. *J. IEST* **2003**, *46*, 98–102. (45) Narcisi, R. S.; Bailey, A. D. Mass Spectrometric Measurements of Positive Ions at Altitudes from 64 to 112 Kilometers. *J. Geophys. Res.* **1965**, *70*, 3687–3700.

(46) Shahin, M. M. Mass-Spectrometric Studies of Corona Discharges in Air at Atmospheric Pressures. J. Chem. Phys. 1966, 45, 2600–2605.

(47) Pavlik, M.; Skalny, J. D. Generation of [H3O]+.(H2O)n Clusters by Positive Corona Discharge in Air. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1757–1766.

(48) Markovitch, O.; Agmon, N. Structure and Energetics of the Hydronium Hydration Shells. J. Phys. Chem. A 2007, 111, 2253–2256.

(49) Sobolewski, A. L.; Domcke, W. Hydrated Hydronium: A Cluster Model of the Solvated Electron? *Phys. Chem. Chem. Phys.* **2002**, *4*, 4–10.

(50) Sobolewski, A. L.; Domcke, W. Ab Initio Investigation of the Structure and Spectroscopy of Hydronium-Water Clusters. J. Phys. Chem. A 2002, 106, 4158-4167.

(51) Agmon, N. The Grotthuss Mechanism. Chem. Phys. Lett. 1995, 244, 456-462.

(52) Lee, D. H.; Choi, C. H.; Choi, T. H.; Sung, B. J.; Kang, H. Asymmetric Transport Mechanisms of Hydronium and Hydroxide Ions in Amorphous Solid Water: Hydroxide Goes Brownian while Hydronium Hops. J. Phys. Chem. Lett. **2014**, *5*, 2568–2572.

(53) Mohammadi, S. S.; Brennan, M.; Oberoi, A.; Vagh, H.; Spencer, M.; Kumar, T. J. D.; Andrews, J. Density Functional Theory and *ab Initio* Molecular Dynamics Investigation of Hydronium Interactions with Graphene. *Energy Procedia* **2017**, *110*, 518–522.

(54) Yin, J.; Zhang, Z.; Li, X.; Zhou, J.; Guo, W. Harvesting Energy from Water Flow over Graphene? *Nano Lett.* **2012**, *12*, 1736–1741.

(55) Iuchi, S.; Chen, H.; Paesani, F.; Voth, G. A. Hydrated Excess Proton at Water-Hydrophobic Interfaces. *J. Phys. Chem. B* **2009**, *113*, 4017–4030.

(56) Zimmermann, R.; Freudenberg, U.; Schweiß, R.; Küttner, D.; Werner, C. Hydroxide and Hydronium Ion Adsorption — A Survey. *Curr. Opin. Colloid Interface Sci.* **2010**, *15*, 196–202.

(57) Cole, D. J.; Ang, P. K.; Loh, K. P. Ion Adsorption at the Graphene/Electrolyte Interface. J. Phys. Chem. Lett. 2011, 2, 1799–1803.