Electronic Supplementary Information

Proton transfer at subkelvin temperatures

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## Table of Contents

## S1    Experimental Details

Neutral HNDs are formed by supersonic expansion of pre-cooled helium (Linde, purity 99.9999 %, stagnation pressure 20 bar) through a nozzle (5.7 μm diameter, temperatures 9.7 K for experiments with $CH_4$ or 9.2 K for experiments with valine) into vacuum. At these conditions the HNDs will contain an average of about $N = 2\times10^5$ helium atoms ($CH_4$) or $9\times10^5$ helium atoms (valine) but the size distribution will be broad.[1] The expanding beam is skimmed by a conical skimmer (Beam Dynamics, Inc.) and ionized by electrons at 70 eV. The electron emission current was 620 μA, resulting in multiple collisions between HNDs and electrons and highly charged droplets.[2] The resulting $He_N^{z+}$ ions are accelerated through a potential drop $\Delta V = 415$ V ($CH_4$) or 570 V (valine) into an electrostatic quadrupole bender. Ions that are transmitted have a specific size-to-charge ratio $N/z$. We chose $N/z = 1.5\times10^5$ and $1.7\times10^5$ for experiments with methane and valine, respectively.

Hydrogen gas is introduced into the vacuum chamber that houses the quadrupole bender (see Fig. 1 in the main text). The pressure, measured with a cold cathode ionization gauge (Pfeiffer model IKR 251), was $4.8\times10^{-4}$ Pa (all pressure values are corrected for the sensitivity of the ion gauge which is specified as 2.4 for $H_2$, 0.7 for $CH_4$, and 5.9 for helium). $H_2$ molecules colliding with a z-fold charged HND will be captured, resulting in the growth of $z$ hydrogen cluster ions $(H_2)_mH^+$, and evaporation of helium atoms from the droplet.

Following the quadrupole bender the doped droplets pass through a pickup cell (length 5 cm) where they collide with proton acceptor molecules, either methane ($CH_4$, Linde, purity 5.5) or D-valine ($C_5H_{11}NO_2$, nominal mass 117 u, grade BioUltra, 99.5%, Sigma-Aldrich). The $CH_4$ pressure in the cell was $7\times10^{-4}$ Pa. Valine was vaporized in the cell at a nominal temperature of 410 K. At that temperature, its vapor pressure extrapolated from experimental values measured at higher temperatures is about $2\times10^{-4}$ Pa,[3] but the accuracy of our temperature measurement, and of the extrapolated values, is difficult to estimate.

The doped droplets that exit the pickup cell pass through three regions in which they are guided by a radio frequency (RF) field. The first one, a RF hexapole (length $L = 26$ cm), is filled with helium gas at 300 K. Collisions between the charged HND and the gas will cause evaporation of He. Further collisions will strip them of $H_2$ molecules and, eventually, lead to shrinkage of the dopant cluster ions. Multiply charged clusters will, at some point, undergo fission; their fate will be discussed in Section S3.

The following two ion guides, a quadrupole mass filter and a differentially pumped RF-hexapole collision cell, were not used in the present work. The ions were then extracted into a commercial time-of-flight mass spectrometer equipped with a double reflectron in W configuration and a microchannel plate (MCP) detector (Micromass Q-TOF Ultima mass spectrometer, Waters). $CH_4$ spectra were recorded in the W-mode and valine spectra in the V-mode. The mass resolution was 3000 at 264 u.

Mass spectra were evaluated by means of a custom-designed software that corrects for experimental artifacts such as background signal levels, non-gaussian peak shapes and mass drift over time[4] The routine takes into account the isotope pattern of all ions that might contribute to a specific mass peak by fitting a simulated spectrum with defined contributions from specific atoms to the measured spectrum in order to retrieve the abundance of ions with a specific stoichiometry.

For measurements with $CH_4$ (Figures 2a and 2b) the He pressure in the collision cell was $p_{He} = 0.178$ Pa, for valine (Figures 3a and 3b) it was $p_{He} = 0.224$ Pa.

## S2    The Energetics of Ion-Molecule Reactions in HNDs

In this section we will estimate the energies released in reactions 3 to 6, the secondary reactions initiated by this energy release, and competing reactions. The charged HNDs are mass-to-charge-selected by the

quadrupole bender; their size-to-charge ratios are $N/z = 1.5 \times 10^5$ and $1.7 \times 10^5$ for droplets to be doped with $CH_4$ and valine, respectively. The main aim here is to show that these HNDs are sufficiently large to dissipate the energy released upon capture of multiple $H_2$ plus $CH_4$ or valine molecules. For the sake of clarity we will consider ions that are singly charged ($z = 1$); the fate of multiply charged HNDs will be addressed in Section S3.

The cohesive energy of bulk helium (isotopically pure $^4$He, to be exact) equals 0.616 meV/atom.[5] Thus we assume $D_{He} \sim 0.616$ meV for the evaporation energy of large HNDs, whether neutral or charged, doped or undoped. An energy of 1 eV released in a reaction will lead to the evaporation of about 1620 He atoms from the HND. The estimate neglects the average kinetic energy carried away by helium atoms that evaporate from a HND at 0.37 K, $E_{kin} = 3/2\, k_B T \sim 0.048$ meV. It also neglects the possible direct ejection of reaction products, or consequences of non-thermal loss of He.

A collision between a HND (neutral or charged) and a gas-phase molecule X in the pickup cell leads to capture of X with a near-100% probability.[6] X will quickly (within some 10 ns) move into the interior of the superfluid droplet ($H_2$, $CH_4$, or valine are not among the small number of species that are heliophobic). If the HND is charged or pre-doped, X will coagulate or react. The collision and subsequent coagulation/reaction will release energy $E^*$ that has three contributions:

$$E^* = E_{coll} + E_{int} + E_{reac} \tag{S1}$$

where $E_{coll}$ is the sum of kinetic energies of the collision partners in the center-of-mass reference frame, $E_{int}$ is the internal thermal energy (rotational + vibrational) energy of X, and $E_{reac}$ is the energy released upon coagulation or reaction.

The mass of the droplet which moves at drift speed $v_d$ through the pickup cell is much larger than the mass $m$ of X, i.e. the center of mass moves at speed $v_d$. $E_{coll}$ would equal $2\, k_B T$ if the droplet were at rest (where $k_B$ is the Boltzmann constant and $T$ the temperature of the gas). For a droplet moving through the thermal gas at speed $v_d$ one obtains[7]

$$E_{coll} = 2k_B T + mv_d^2/2 \tag{S2}$$

The speed $v_d$ depends on the temperature of the nozzle[1] and the electrostatic potential difference between the ionizer region and the pickup cell. The values are $v_d = 569$ and 647 m/s for experiments with $CH_4$ and valine, respectively. Thus, in experiments with $CH_4$, each collision with $H_2$ or $CH_4$ (which are both at 300 K) adds $E_{coll} = 55$ and 79 meV, respectively. In experiments with valine (temperature 410 K) the corresponding values are 56 and 323 meV.

The vibrational degrees of freedom in $H_2$ and $CH_4$ are essentially frozen at 300 K,[9] hence their internal energies $E_{int}$ equal approximately $k_B T = 26$ and 1.5 $k_B T = 39$ meV, respectively. For valine at 410 K, we estimate $E_{int} \sim 510$ meV from measurements involving crystalline valine.[10]

We proceed to estimate the energetics of specific ion-molecule reaction. Capture of the first $H_2$ molecule results in the reaction

$$He_2^+ + H_2 \rightarrow He_2 + H_2^+ \tag{S3}$$

which will release a total of approximately 6.88 eV, the difference between the adiabatic ionization energies of $He_2$ (22.223 eV) and $H_2$ (15.426 eV)[11] plus $E_{coll} + E_{int} = 0.081$ eV. About $1.1 \times 10^4$ He atoms (equivalent to 7 % of the total) will be evaporated. Note that the energy release greatly exceeds the bond strength (2.7 eV) of $H_2^+$, hence ejection of an atomic H from the doped HND is conceivable. However, the bond length of $He_2^+$ is only 0.105 nm,[11] much less than that of $He_2$, hence vertical electron transfer from $H_2$ to $He_2^+$ results in a highly compressed $He_2$ molecule. Hence, ejection of a fast He atom is the more likely consequence of reaction S3, and much less than 7 % of He would be evaporated.

Capture of a second $H_2$ results in

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{S4}$$

which releases a total energy of about 1.8 eV, equivalent to the loss of approximately 2900 He atoms, or 2 % of the initial value. H is heliophobic; inside a HND it would reside in a large cavity,[12] and it will probably be expelled. The HND could conceivably quench the escape of H but experiments in which $H_2$-doped HNDs are ionized by electrons show a rather small signal of even-numbered $H_n^+$ cluster ions.[13] Tachikawa has studied vertical ionization of $H_2$ inside a small, bare $H_2$ cluster by ab-initio dynamics calculations.[14] He also finds that a fast H atom will be ejected.

Capture of further $H_2$ and growth of a $(H_2)_m H^+$ cluster ion will continue to release significant amounts of energies as long as $m$ is small. Nearly 2 eV (including the contributions from $E_{coll} + E_{int}$) will be released upon cluster growth from $m = 1$ to 11.[15, 16] By that time the fourth solvation shell has been completed, and the energy release upon further captures will quickly converge to about 0.086 eV, the sum of the average collision energy,

the internal energy of $H_2$, and the cohesive energy of bulk hydrogen (4.8 meV), causing the evaporation of a mere 140 He atoms per collision.

In the pickup cell, the $H_2$-doped HNDs will collide with X = methane or valine. The first collision

$$(H_2)_mH^+ + X \rightarrow (H_2)_m + XH^+ \tag{S5}$$

releases the difference between the proton affinities (PAs) of $CH_4$ (5.633 eV) or valine (9.438 eV) and that of $(H_2)_m$, plus $E_{coll} + E_{int}$. $E_{int}$ can be estimated from the temperature dependences of the molar heat capacities of $CH_4$ and valine.[9, 10] One finds $E_{coll} + E_{int} = 0.120$ and 0.830 V for $CH_4$ and valine, respectively. If $m = 1$, the total energy released in reaction S5 will be 4.50 and 5.21 eV for $CH_4$ and valine, respectively. This will cause the evaporation of about 2200 and 9600 He atoms for $CH_4$ and valine, respectively. For $m > 1$ the corresponding values will be smaller because the PA of $(H_2)_m$ exceeds that of $H_2$.

The energy released in the final reaction

$$X_nH^+ + X \rightarrow X_{n+1}H^+ \tag{S6}$$

equals the sum of $E_{coll}$, $E_{int}$, and the energy released up cluster growth. The dissociation energy of $CH_4CH_5^+$ equals $E_{reac} = 0.30$ eV;[17] that of various amino acid proton-bound dimers is about 1.2 eV.[18, 19] Hence $E^*$ equals about 0.42 and 2.03 eV for formation of the protonated methane and valine dimer, respectively; equivalent to the evaporation of some 680 or 3300 He atoms. For large values of $n$, $E_{reac}$ will gradually converge to the bulk cohesive energy which equals approximately 0.085 eV for $CH_4$ and 1.7 eV for valine.[3, 17] The total energy release will then amount to about 0.18 eV for an added $CH_4$, and 2.3 eV for an added valine, equivalent to the loss of 330 or 4100 He atoms for $CH_4$ and valine, respectively.

In conclusion, large amounts of energy are released in some of the reactions considered, especially upon electron transfer from $H_2$ to $He_2^+$, and proton transfer from $(H_2)_mH^+$ to X = $CH_4$ or valine. Still, the number of helium atoms evaporated as a result of these reactions would be well below 10 % of the initial size of the HND. Furthermore, highly exothermic reactions are likely to lead to nonthermal ejection of reaction products, thus reducing the energy that needs to be dissipated by evaporation of He atoms.

Following the pickup cell the doped HNDs pass through the collision cell (length $L = 26$ cm) filled with He at 300 K. Each collision will transfer approximately $E^* = E_{coll} = 0.06$ eV, causing the evaporation of some 100 He atoms. The relations discussed in Section S3 may be used to estimate the path length $L_1$ after which a doped HND will have shed all of its He atoms. Over the remaining path $L_2 = L - L_1$ the ion will then shed excess $H_2$, producing bare $X_nH^+$ ions, and evaporate monomers X. This process is illustrated by the mas spectra shown in Fig. 4 of the main text.

**S3   The Fate of Multiply Charged HNDs**

Shrinkage of a $z$-fold charged HND will result in spontaneous charge separation (fission) once its size drops below its critical size for that charge state.[2] A droplet with an initial charge state $z_i$ close to the maximum number $z_{max}$ of charges that it can accommodate will, upon doping, quickly shrink to a size where it ejects a monocation complexed with a very small number of He atoms, plus a large, doped HND with $z_i-1$ charge centers. This process may occur several times in the pickup cell or, if $z_i \ll z_{max}$, not at all. But in the collision cell $N/z$ will definitely drop below the critical value of $5\times10^4$ for doubly charged droplets, and only singly charged doped HNDs will remain.

The primary product of electron ionization of a pure HND is $He^+$. In an undoped droplet the charge may move by resonant charge transfer but eventually the process is terminated by formation of a tightly bound $He_2^+$.[6] The high electron emission current in our experiment (620 µA) will result in multiple inelastic collisions between a given HND and the primary electrons, resulting in highly charged droplets. Charge states $z$ as large as 55 have been reported for droplets.[2] The $z$ $He_2^+$ ions will reside near the surface because of their mutual Coulomb repulsion. Upon multiple capture of $H_2$, the charge centers will transform into $(H_2)_mH^+$ where, on average, $m+1$ will equal the number of captured species divided by $z$. In the pickup cell, $n$ molecules X = methane or valine will be added to each charge center where, on average, $n$ will equal the number of captured species divided by $z$.

The minimum size of a $z$-fold charged, undoped HND equals $N_z = 3.54\times10^4 z^{3/2}$.[2] This relation will also apply to doped droplets as long as the volume occupied by the dopant(s) is much less than the volume occupied by the $N$ He atoms. Once $N$ declines below $N_z$ (as a result of collisions with $H_2$ or with X = $CH_4$ or valine in the pickup cell), it will undergo spontaneous fission into a very small singly charged helium cluster containing fewer than about $10^2$ atoms, plus a $z-1$ fold HND with a size of approximately $N_z$.[2, 20]

In the present experiment the quadrupole bender was set to transmit ions with $N/z = 1.5\times10^5$ and $1.7\times10^5$ for methane and valine, respectively. The corresponding maximum charge states are 17 and 23, respectively. For an illustration of the sequence of events, we consider a HND with $N/z = 1.5\times10^5$ in an initial charge state

$z = 16$, containing $N = 2.4\times10^6$ He atoms. It becomes unstable with respect to fission once $N$ drops below $N_{16}$ $= 2.27\times10^6$, i.e. after loss of $1.3\times10^5$ He atoms. This requires an energy release of 80 eV. Reaction S3 releases close to 7 eV. More than 80 eV will have been released even before all 16 $He_2^+$ charge centers have been converted to $H_2^+$, and the HND will undergo spontaneous fission into a 15-fold doped HND of size $N = 2.27\times10^6$. If the partial $H_2$ pressure is sufficiently high, the droplet will capture many more $H_2$, undergo reaction S3 a few more times, and reaction S4 many more times. The HND may undergo further fission events before it exits the vacuum chamber filled with $H_2$ gas.

The fate of a z-fold charged HND in the $H_2$ pickup cell may be estimated as follows: The capture cross section $\sigma$ of the droplet equals the hard-sphere value

$$\sigma = \pi(R_d + R_s)^2 = \pi(R_{He}N^{1/3} + R_s)^2 = \pi R_{He}^2(N^{1/3} + R_r^{-1})^2 \tag{S7}$$

where $R_d$ is the radius of the droplet which contains $N$ He atoms, $R_{He}$ and $R_s$ are the effective radii of He and the scatterer $H_2$, and $R_r = R_{He}/R_s$ characterizes the size of He relative to that of $H_2$.

The droplet moves at speed $v_d$ through the scattering gas. $v_d$ may be computed from the speed of the undoped neutral HNDs which depends on the nozzle temperature, and the acceleration of the charged HNDs in the applied electrostatic field. In the present work, $v_d = 569$ and 647 m/s for experiments with methane and valine, respectively.

The collision frequency $f$ equals

$$f = n_s v_r \sigma \tag{S8}$$

where $n_s$ is the number density of the $H_2$ scatterers which move at velocity $v$, and $v_r$ is the average relative collision speed in the center-of-mass system i.e. $|v\text{-}v_d|$ integrated over the surface of the droplet, all incident angles, and the thermal speed distribution of the scattering gas. The averaging can be simplified by noting that the asymptotic limit of $f$ equals $n\sigma v$ if the droplet moves slowly ($v_d \ll v$), and $n_s\sigma v_d$ if the droplet moves fast (because the droplet sweeps a volume $\sigma L$ within time $L/v_d$). We interpolate between the asymptotic limits with the expression

$$v_r \approx (v^2 + v_d^2)^{1/2} \tag{S9}$$

The number $dx$ of collisions with $H_2$ over a short path $dL$ may be written

$$dx = \frac{1}{\lambda}dL = \frac{f}{v_d}dL = n\sigma\frac{v_r}{v_d}dL \tag{S10}$$

where $\lambda$ is the mean free path of the HND moving through the scattering gas.

Each collision releases an energy $E^*$ (see eq. S1), resulting in the evaporation of $E^*/D_{He}$ helium atoms, hence the change in droplet size after $dx$ collisions equals

$$dN = -(E^*/D_{He})dx \tag{S11}$$

which can be combined with eqs. S7 and S10 to write

$$(N^{1/3} + R_r^{-1})^{-2}dN = -n\pi R_{He}^2\frac{v_r E^*}{v_d D_{He}}dL \tag{S12}$$

Integration provides the relation between droplet size and path length provided $E^*$ is constant. If that assumption fails one has to compute $dL$ for each collision. For each initial charge state z, one can thus estimate the charge state and average size of the embedded $(H_2)_mH^+$ when the HND exits the vacuum chamber that houses the quadrupole bender. Note that each $z_1$-fold charged HND that enters this section produces one $z_2$-fold charged HND that exits. The small singly charged fragments that result from fission are of no interest because they do not have enough cooling power to capture additional molecules. Upon further collisions they will evaporate their constituents and end up as monomers or very small molecular ions and be lost on their way through the RF ion guides.

The fate of a $z_2$-fold charged HND containing $z_2$ $(H_2)_mH^+$ ions (where the average value of $m$ is known) in the pickup cell can be modeled as described above but now $v$, $n_s$ and $R_s$ now refer to the scatterer methane or valine.

In the collision cell the doped HND will lose all of its helium and along the way fission until $z = 1$ (the minimum size of a doubly charged HND equals $N_2 = 1\times10^5$). It will also lose all or some of its $H_2$, and possibly some molecules X. The relations described above may be applied again, but now the quantities $v$, $n_s$ and $R_s$ refer to helium, and eq. S1 simplifies to $E^* = E_{coll}$. Furthermore, Eq. S7 needs to be modified when $N$ becomes small and the contribution of the embedded dopant(s) to the total volume of the HND is no longer negligible.
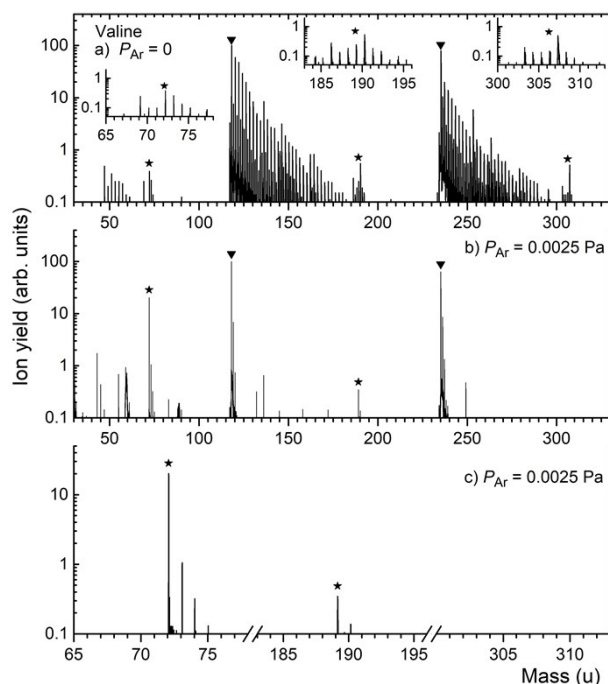
## S4  Mass Spectra of Valine Clusters



Fig. S1 Two mass spectra of valine clusters. The top panel reproduces the spectrum from Fig. 3a: Helium atoms were completely stripped from the doped HNDs, but some $H_2$ molecules remained attached to $V_nH^+$. Panel b displays a spectrum recorded after further dissociation was induced by collisions with argon gas in the last of the three ion guides (argon pressure 0.0025 Pa, collision energy 25 eV in the lab system). Triangles and asterisks mark the positions of $V_nH^+$ and $[V_n\text{-COOH}]^+$ ions, respectively. Panel c zooms into the same mass regions as the insets in panel a.

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