Supporting Information:

Core and Valence Level Photoelectron Spectroscopy of Nanosolvated KCl

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Details of the spectra

Table S1: Table of clustering conditions and number of recorded scans. \( T_P(\,^\circ\text{C}) \) is given to 5 °C accuracy.

|       | \( T_L(\,^\circ\text{C}) \) | \( T_N(\,^\circ\text{C}) \) | P(mbar) | \( \langle N \rangle \) | \( T_P(\,^\circ\text{C}) \) | \( \langle k \rangle \) | \( \#\text{scans} \) | \( \#\text{scans} \) |
|-------|---------------------|---------------------|-------|---------------------|---------------------|---------------------|---------------------|---------------------|
| \( \text{H}_2\text{O} \) | 80 | 100 | 500 | 160 | - | 0 | 18 | - |
| \( \text{H}_2\text{O} \) | 80 | 100 | 500 | 160 | 485 | 0.5 | 4 | - |
| \( \text{H}_2\text{O} \) | 80 | 100 | 500 | 160 | 510 | 1.5 | 3 | 15 |
| \( \text{H}_2\text{O} \) | 80 | 100 | 500 | 160 | 530 | 3.4 | 3 | 15 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | - | 0 | 5 | - |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 485 | 1.1 | 7 | 40 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 495 | 1.7 | 3 | 40 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 505 | 2.6 | 3 | 35 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 545 | 13 | 2 | 29 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 560 | 22 | 3 | 20 |
| \( \text{H}_2\text{O} + \text{Ar} \) | 80 | 100 | 1000 | 500 | 580 | 46 | 5 | 5 |

Peak analysis

The 1b\(_1\) VBE of water clusters was fitted with a single symmetric Gaussian. Here the background reference spectrum was fitted first with a set of peaks describing the vibrational fine structure of water\(^1\) and the minor contribution from vacuum impurities. These curve shapes were then used to account for their contribution in the cluster spectra. The 3a\(_1\) peak of condensed water is considered split and typically described with two peaks,\(^2\) but as here we are mainly interested in the 1b\(_1\) feature, a single peak was used for simplicity to account for the partial overlap with 1b\(_1\). Additional necessary constraints were applied to relative positions and ratios of the peaks for the fitting algorithm to produce physically meaningful results.

The Cl3p and K3p features were fitted with symmetric Gaussian profiles. Single peak fits were used for simplicity and they mostly reproduce the observed features well. The pure water cluster spectra were first fitted separately and this result was then used as a starting point of the mixed spectra fits for the low concentrations.
For Cl 2p, the peak intensity ratio between the 2p$_{1/2}$ and 2p$_{3/2}$ components was fixed to the statistical state degeneracy 1:2. The spin-orbit splitting of the monomer peaks and the cluster peaks was found to be $\sim 1.6$ eV, similar to e.g. in refs. 3, 4, and this value was fixed for all (monomer, dimer and cluster) components to improve the fit quality and consistency. Lorentzian broadening was fixed to 100 meV for all Cl 2p peaks to account for lifetime broadening.$^5$ The Gaussian widths were forced to be the same for both spin-orbit components. The energy positions, intensities and Gaussian widths were otherwise left as free parameters in the fits.

The monomer and dimer peaks overlapping with the mixed cluster peaks were accounted for when necessary (with some additional constraints when their countrate was low). As a side result, their VBEs can be extracted from the highest temperature spectrum in which we assume a negligible contribution from clusters. The VBEs of KCl and [KCl]$_2$ are 8.9$\pm$0.1 eV & 9.7$\pm$0.1 eV for Cl 3p, 25.1$\pm$0.1 eV & 24.1$\pm$0.1 eV for K 3p and 202.2$\pm$0.1 & 202.8$\pm$0.2 for Cl 2p$_{3/2}$, respectively.

**Pick up estimation**

The probability for a water cluster to pick up $k$ salt molecules follows the Poisson distribution

$$P(k) = \frac{(k)^k}{k!} e^{-\langle k \rangle}.$$  

(1)

The expectation value $\langle k \rangle$, i.e. the mean number of picked up molecules, is

$$\langle k \rangle = \rho \cdot \sigma \cdot L = \frac{p(T)}{k_B T_P} \cdot \sigma \cdot L,$$  

(2)

where $\sigma$ is the pick-up cross section, $L$ is the length of the pick up cell, $\rho = p/(k_B T_P)$ is the number density of KCl, $p$ is the vapor pressure of KCl and $T_P$ is the temperature of KCl.$^6$ It turns out that given the uncertainties in determining the effective $\sigma$,$^7,8$ $L$ and $\rho$, direct
application of this equation is not justified. We therefore estimate $\langle k \rangle$ from the observed fall of the water cluster signal intensity, which occurs due to evaporative cooling of the clusters and due to diffusion losses, and therefore correlates with the true amount of occurring pick up. The relative peak height (counts at peak maximum per scan) of the $1b_1$ valence band for the smaller clusters (due to its higher sensitivity to both diffusion and evaporation) is plotted as a function of pick up temperature in figure S1 (red circles).

![Figure S1: Temperature dependent $1b_1$ intensity drop of the smaller cluster size together with calculated P(0) using $\langle k \rangle$ from equations 2 (theor.) and 3 ($f$ corrected).](image)

A maximum possible intensity drop occurs if it is assumed that none of the clusters with $k \geq 1$ are observed. In this case, the cluster intensity should follow P(0) (eq. 1). The calculated P(0) according to eq. 1 is shown by the dashed line, using the length of the pick up cell $L=12.5\,\text{mm}$ and a geometrical cross section of the water cluster $\sigma = 358\,\text{Å}^2$ (calculated as in ref.\textsuperscript{9} and refs. therein). The calculation is clearly an underestimation. There are several possible reasons for this, including slight inaccuracy in the temperature measurement and $L$ and $\sigma$ being effectively larger.\textsuperscript{7} Therefore, we simplify eq. 2 to

$$\langle k \rangle = \frac{p(T)}{T_P} \cdot f. \quad (3)$$

Here the scaling of $\langle k \rangle$ with the changing temperature is retained, and $f$ is a constant that accounts for the effective $\sigma$ and $L$ (and $1/k_B$) as well as uncertainties of the measured $T_P$. 

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and correspondingly calculated\textsuperscript{10} $p(T)$. By selecting $f$ to match with the observations (solid black line in fig. S1), a lower limit of true $\langle k \rangle$ is obtained, being $\sim$25 times larger than calculated according to eq. 2. This approach bypasses the need for accurate knowledge on the different parameters in eq. 2. Yet, acknowledging the crudeness of the estimation, the discussion has been accordingly kept at a qualitative level. To account for the increasing pick up probability with increasing cluster size, eq. 3 is further multiplied with $\sigma_L/\sigma_S = 2.1$, where $\sigma_L$ and $\sigma_S$ are the geometrical cross sections of the clusters calculated for $N = 500$ & $N = 160$, respectively.

**Temperature change of the clusters**

Crude estimations for the internal energy changes involved in the pick up process are presented. Since the cluster beam contains a distribution of cluster sizes, the estimated temperature change of a water cluster upon a pick up event and upon evaporation of water are plotted as a function of cluster size $N$ in figure S2. The curves assume that the energy change is fully transformed to internal heat of the cluster. The temperature change of a water cluster is calculated as

$$\Delta T \sim \frac{\Delta H}{(C_m N)},$$

where $\Delta H$ is the internal energy change, $C_m$ is the heat capacity per molecule and $N$ is the number of water molecules. In general, $C_m$ depends on cluster size and temperature,\textsuperscript{11} but for simplicity we use a representative value of 0.25 meV/K/molecule. The binding enthalpy of an evaporating water molecule likewise depends on cluster size and composition, and we use a representative value of 500 meV for the plot, which is also between the values in bulk liquid water and bulk water ice.\textsuperscript{12}
Figure S2: Temperature change of a water cluster in a single pick up event accounting for the collision or the combined collision + solvation energies. The temperature change upon evaporation of a single water molecule is also shown.

The mean collision energy between a water cluster and a free KCl molecule is\textsuperscript{13,14}

\[
\langle E_{col} \rangle = 2k_B T + \frac{3}{2} k_B T + \frac{1}{2} m v^2,
\]  

(5)

where \( T \) is the temperature of the salt, \( m \) is the mass of KCl and \( v \) is the cluster beam velocity. The first term accounts for the internal energy (vibrational + rotational) of KCl and the latter two account for the kinetic energy. The kinetic part assumes a Maxwellian velocity distribution for KCl and a sharply peaked velocity for the clusters. The cluster velocity was calculated similarly as described e.g. in ref. 9. Eq. 5 results to \( \sim 500–800 \) meV, where variation is due to slightly different cluster beam velocities and the temperature range of the salt. The curves in fig. S2 are plotted using a value of 500 meV.

The energy release in the solvation of a single KCl molecule from the gas phase is calculated as a sum of enthalpy of dissociation of

\[ KCl(g) \rightarrow Cl^-(g) + K^+(g) \quad (481.2 \text{kJ/mol}^{15}) \]

and subsequent hydration enthalpies

\[ K^+(g) \rightarrow K^+(aq) \quad (-322 \text{kJ/mol}^{16}) \]
\[ \text{Cl}^- (g) \rightarrow \text{Cl}^- (aq) \quad (-381 \text{kJ/mol}^{16}) \]

This adds to -222 kJ/mol \(\sim -2.3 \text{ eV} \).

**Photoelectron spectra measured with hv=100 eV**

![Photoelectron spectra graph](image)

Figure S3: A broader view of the low BE spectra. A few vacuum impurity features are indicated with the thick vertical lines at the bottom.

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