I. EXPERIMENTAL DETAILS

Photoemission measurements of aqueous sodium chloride solutions were performed from a 22-µm sized liquid microjet in vacuum at the soft-X-ray U41 PGM undulator beamline of BESSY, Berlin. The jet velocity was approximately 60 m s\(^{-1}\), and the starting temperature was 8 °C. The jet temperature in the interaction region is not expected to be less than approximately 3 °C as determined by evaporative cooling modeling.\(^1,2\)

Experimental details of the liquid microjet technique and the setup have been described elsewhere.\(^3-5\) Briefly, electrons were detected normal to both the synchrotron light polarization vector and the flow of the liquid jet. Photoelectrons pass through a 150-µm diameter orifice which separates the main interaction chamber (10\(^{-4}\) mbar pressure under operation conditions) from the differentially pumped detector chamber (10\(^{-7}\) mbar), housing a hemispherical electron-energy analyzer. The entrance to the analyzer is at an approximately 0.5 mm distance from the liquid jet—a short enough distance to ensure that detected photoelectrons have not suffered from inelastic scattering with water gas-phase molecules around the small-sized liquid jet.\(^3-5\) The energy resolution of the U41 beamline is better than 50 meV at 200 eV photon energy used here, and the energy resolution of the hemispherical energy analyzer is constant with kinetic energy (about 100 meV at 10 eV pass energy). The small focal size, 23 × 12 µm\(^2\), of the incident photon beam allows for matching spatial overlap with the liquid microjet, reducing the gas-phase contributions of the measured spectra to less than 5% for liquid water.

II. COMPUTATIONAL DETAILS

First-principles molecular-dynamics (MD) trajectories were taken from Ref. 6. They were obtained using the PBE0 functional and the bisecting algorithm (threshold of 0.02) proposed in Ref. 7. The MD cell contained 52 water molecules, one Na and one Cl atom. After initial ~3–4-ps equilibration at 380 K using the Bussi–Donadio–Parrinello thermostat\(^8\) (time constant \(\tau\) varied between 60 and 120 fs), the solution was simulated for 25 ps in the NVT ensemble at the same temperature (\(\tau\) varied in the range of 120 and 240 fs). We performed two independent runs starting with uncorrelated snapshots to increase the accuracy of our analysis. Simulations were carried out using the \textit{Qbox} code.\(^9\) The forces acting on atoms were computed at a kinetic energy cutoff of 85 Ry, using Hamann–Schlüter–Chiang–Vanderbilt (HSCV) pseudopotentials\(^10\) for H, O, and Cl atoms, and Troullier–Martins pseudopotential for the Na atom. Deuterium atoms were used instead of hydrogen to take advantage of a larger simulation time step of 0.363 fs.
III. SINGLE-PARTICLE ENERGY LEVELS FROM DENSITY FUNCTIONAL THEORY AND MANY-BODY PERTURBATION THEORY

The electronic properties of solutions at the density-functional theory (DFT) level were computed using the quantum espresso code.\textsuperscript{11} We set the kinetic energy cutoff to 85 Ry and used HSCV pseudopotentials for H and O atoms, and optimized norm-conserving pseudopotentials (ONCV)\textsuperscript{12} for Na and Cl atoms.\textsuperscript{10} Both 2s and 2p electrons of Na were treated as valence electrons in our computations of single-particle states.

\( G_0W_0 \) calculations were performed with the west code,\textsuperscript{13,14} starting from PBE, PBE0, RSH,\textsuperscript{15} and sc-hybrid\textsuperscript{16} wavefunctions. For each of those methods, quasiparticle energies were determined using exactly the same exchange-correlation potential as the one employed in the self-consistent-field procedure. All our \( G_0W_0 \) calculations were carried out with 1600 eigenpotentials.\textsuperscript{13}

DFT and \( G_0W_0/PBE \) calculations were carried out for 128 equally-spaced snapshots along each of the two 25-ps trajectories. \( G_0W_0 \) calculations started from hybrid functionals were instead performed for 4 snapshots. For the former group of methods, the values reported in this work were always averages, while for the latter group of methods, only one representative snapshot was analyzed due to similarity of results obtained for the 4 different samples.

IV. ABSOLUTE ORBITAL ENERGIES REFERENCED TO VACUUM

Total and single-particle energies computed within a plane-wave pseudopotential formalism are defined up to an additive constant.\textsuperscript{17–19} Hence they cannot be directly compared to experimental binding energies referred to vacuum.\textsuperscript{20}

In order to compare our results with experiments, we first determined the plane-average electrostatic potential of a water slab—a layer of liquid in contact with a relatively thick region of vacuum. The plane-average electrostatic potential is defined as follows:

\[
\bar{V}(z) = \frac{1}{A} \left\langle \int \int V(x, y, z) \, dx \, dy \right\rangle,
\]

where \( z \) is the direction perpendicular to the water surface and \( A \) is the surface area of the slab. Following the computational protocol of Ref. 21, we simulated water slabs using the TIP3P force field in a supercell with dimensions of 12.77 \( \times \) 12.77 \( \times \) 80 å containing 108 molecules. As discussed in Ref. 21, the computed average potentials obtained from Eq. (1) were weakly dependent on the water force field used in slab simulations, with differences on the order of 0.1 eV between SPC/E, TIP3P, and TIP4P interatomic potentials. Our molecular dynamics simulations were run in the NVE ensemble for 5 ns after equilibration at 300 K for 1 ns, using the GROMACS code.\textsuperscript{22} We computed the electrostatic potentials from electron densities obtained with all density-functional methods used in this work. DFT calculations were performed for 256 equally-separated snapshots extracted from the slab simulation. The resulting plane-average electrostatic potentials are summarized in Figure S1.

The energy levels \( \tilde{\varepsilon}_i \) aligned to vacuum where obtained from the energy levels computed in our bulk calculations \( \varepsilon_i \) as follows:

\[
\tilde{\varepsilon}_i = \varepsilon_i - \Delta V_{\text{slab}} - V_{\text{bulk}},
\]

where \( \Delta V_{\text{slab}} = V_{\text{vacuum}}^{\text{slab}} - V_{\text{water}}^{\text{slab}} \) is the difference between the electrostatic potential computed in the vacuum region of the slab \( V_{\text{vacuum}}^{\text{slab}} \) and in the region of the slab occupied by water \( V_{\text{water}}^{\text{slab}} \) (see Figure S1). The term \( V_{\text{bulk}} \) is the value of the plane-average electrostatic potential computed for bulk samples. The latter was determined to be 0.155 eV for all functionals employed in our work (all calculations were carried out with the same pseudopotentials and kinetic energy cutoff).
FIG. S1. Plane-average electrostatic potential computed across the interface of a slab composed of 108 water molecules described by the TIP3P model. The slab was centered in the middle of the simulation cell. The arrows indicate the difference in the electrostatic potential in the water ($V_{\text{water, slab}}$) and vacuum regions ($V_{\text{vacuum, slab}}$) of the slab. These values were used in Eq. (2) to compute the shifts of the orbital energies with respect to vacuum (Table SI).

TABLE SI. Sum of values of the electrostatic potentials $\Delta V_{\text{slab}}$ (defined by the arrows in Figure S1) and $V_{\text{bulk}}$ (0.155 eV) used in Eq. (2) for each functional. $G_0W_0$/DFT eigenvalues were aligned with vacuum using respective DFT values.

<table>
<thead>
<tr>
<th>Density functional</th>
<th>$\Delta V_{\text{slab}} + V_{\text{bulk}}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>3.69</td>
</tr>
<tr>
<td>PBE0</td>
<td>3.62</td>
</tr>
<tr>
<td>RSH</td>
<td>3.57</td>
</tr>
<tr>
<td>sc-hybrid</td>
<td>3.53</td>
</tr>
</tbody>
</table>

V. CALCULATION OF DENSITY OF STATES

Orbital energies referenced to vacuum were used for calculation of densities of states (DOS). DOS plots were computed by summing over normalized Gaussians centered at occupied orbital energies:

$$g(\varepsilon) = \frac{1}{\sigma \sqrt{2\pi}} \sum_{i}^{\text{occ.}} e^{-\frac{(\varepsilon - \varepsilon_i)^2}{2\sigma^2}},$$

(3)
where $\varepsilon_i$ is the orbital energy of $i$th orbital and the sum is over all occupied orbitals. For partial densities of states of Na$^+$ and Cl$^-$ ions (gray area in Figures 2–4 of the main text), the occupied orbitals were projected on maximally localized Wannier functions\textsuperscript{23,24} at the positions of the ionic sites. The peak maxima were identified by computing the derivative of Eq. (3) with respect to $\varepsilon$.

The broadening factor $\sigma$ was chosen to be 0.15 eV in DFT and $\text{G}_0\text{W}_0$/PBE calculations. Densities of states computed for all individual snapshots were averaged for each computational method. For $\text{G}_0\text{W}_0$/PBE0, $\text{G}_0\text{W}_0$/RSH, and $\text{G}_0\text{W}_0$/sc-hybrid methods, only 2–4 representative snapshots were used. Figure 4 of the main text shows DOS plot from only one representative snapshot chosen based on similarity to the averaged $\text{G}_0\text{W}_0$/PBE DOS plot. The Gaussian broadening for DOS plots in Figure 4 was set to $\sigma = 0.3$ eV to match the full width at half maximum (fwhm) of DOS plots obtained in DFT and $\text{G}_0\text{W}_0$/PBE calculations.

To compare the agreement between experimental and theoretical binding energies without using absolute energies (the accuracy of which depends on the functional), we computed mean absolute percentage errors (MAPE). MAPE is defined as an average of relative unsigned errors for distances between the $1b_1$ and other peaks in the spectrum ($\Delta_i \equiv E_i - E_{1b_1}$) of theory with respect to experiment:

$$\text{MAPE, \%} = \frac{1}{N} \sum_i \left| \frac{\Delta_i^{\text{theory}} - \Delta_i^{\text{experiment}}}{\Delta_i^{\text{experiment}}} \right| \cdot 100\% \quad (4)$$

In the calculation of MAPE, we took into account all maxima in PE spectra except for Cl 3s, since the position of this peak in measured spectra is uncertain, and there is no reliable experimental reference. The diagram of MAPEs for all the methods/computational protocols we used is summarized in the Figure S2 below:

![Figure S2](image_url)

**FIG. S2.** Mean absolute percentage error (MAPE) of energy differences between the $1b_1$ peak of water and other maxima in photoelectron spectra of a NaCl solution (Table I of the article). Calculations were carried out with density functional approximations (“DFT”) and many-body perturbation theory ($\text{G}_0\text{W}_0$) based on the wavefunctions from the respective DFT methods, as specified on the $x$ axis (see text).
VI. CALCULATION OF PHOTOELECTRON INTENSITIES

We computed intensities of photoelectron spectra \( I(E) \) by combining theoretical spectral lines \( f_i(E; E_i, \Gamma_i) \) with differential cross sections \( d\sigma_i/d\Omega \) for all occupied states:

\[
I(E) \propto \sum_{i}^{\text{occ}} f_i(E; E_i, \Gamma_i) \frac{d\sigma_i(h\nu)}{d\Omega},
\]

where \( h\nu \) is X-ray photon energy, \( E_i \) are electron binding energies, and \( E = h\nu - E_i \) are electron kinetic energies. The spectral lines were represented by Lorentzian functions

\[
f_i(E; E_i, \Gamma_i) = \frac{\Gamma_i}{\pi (E - E_i)^2 + \Gamma_i^2},
\]

where \( E_i \) are quasiparticle energies and \( \Gamma_i \) are spectral linewidths, obtained from the real and imaginary parts of the \( G_0W_0 \) self-energy \( \Sigma_i \), respectively. We verified that the sum of Lorentzian functions is a very good approximation to the full spectral function by comparing the two quantities for one of our molecular configurations. We filtered states with linewidths below 0.3 eV by setting \( \Gamma \) to 0.3 eV.

Within dipole approximation, the differential photoionization cross-sections \( \sigma_i \) are obtained by Cooper–Zare formula\(^{(25)}\)

\[
d\sigma_i/d\Omega = \sigma_i \frac{4\pi}{\Omega} \left[ 1 + \beta_i P_2(\cos \theta) \right],
\]

where \( \theta \) is the angle between the photoelectron velocity and light beam polarization plane, \( P_2(\cos \theta) = (1/2)(3\cos^2 \theta - 1) \) is a second-order Legendre polynomial, and \( \Omega \) is the detection solid angle. The energy-dependent anisotropy parameter \( \beta_i \) ranges between \(-1\) and 2, becoming 0 for isotropic emission.\(^{(3)}\) For the angle \( \theta = \pi/2 \) used in our experimental measurements, Eq. (7) simplifies to:

\[
d\sigma_i/d\Omega = \frac{\sigma_i}{4\pi} \left( 1 - \frac{\beta_i}{2} \right).
\]

In order to evaluate Eq. (8), we used cross-sections and anisotropy parameters of Yeh\(^{(26)}\) for sodium and chlorine atoms computed at 200 eV. For water, we used experimental gas-phase data of Banna \textit{et al.}\(^{(27)}\). Anisotropy parameters for water molecular orbitals were extrapolated to 200 eV. There was not enough data to reliably extrapolate photoionization cross-sections to 200 eV, hence we used values of Ref. 27 measured at the highest energy of 114.7 eV. All \( \sigma_i \) and \( \beta_i \) parameters used in this work are summarized in Table SII.

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TABLE SII. Parameters $\sigma_i$ and $\beta_i$ used in the calculation of differential cross-sections in Eq. (8) for molecular orbitals of water (1$b_1$, 3$a_1$, 1$b_2$, 2$a_1$), as well as atomic orbitals of Na (2s, 2p) and Cl (3s, 3p) as a function of the photon energy $h\nu$.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$\sigma_i$, Mb</th>
<th>$\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$b_1$</td>
<td>0.4$^a$</td>
<td>1.25$^b$</td>
</tr>
<tr>
<td>3$a_1$</td>
<td>0.4$^a$</td>
<td>1.33$^b$</td>
</tr>
<tr>
<td>1$b_2$</td>
<td>0.3$^a$</td>
<td>1.25$^b$</td>
</tr>
<tr>
<td>2$a_1$</td>
<td>0.3$^a$</td>
<td>1.46$^b$</td>
</tr>
<tr>
<td>2s</td>
<td>0.3004$^c$</td>
<td>1.5$^d$</td>
</tr>
<tr>
<td>2p</td>
<td>1.074$^c$</td>
<td>1.12$^d$</td>
</tr>
<tr>
<td>3s</td>
<td>0.1048$^c$</td>
<td>1.5$^d$</td>
</tr>
<tr>
<td>3p</td>
<td>0.2772$^c$</td>
<td>1.21$^d$</td>
</tr>
</tbody>
</table>

$^a$ Total partial cross-sections measured for water vapor at $h\nu = 114.7$ eV.$^{27}$
$^b$ Values derived from extrapolation of experimental anisotropy parameters from gas-phase water.$^{27}$ and reduced by 25% to account for electron elastic scattering in the liquid phase (see Ref. 28).
$^c$ Atomic cross-sections$^{26}$ interpolated to $h\nu = 200$ eV.
$^d$ Atomic anisotropy parameters$^{26}$ interpolated to $h\nu = 200$ eV and reduced by 25% to account for scattering in the liquid phase (see Ref. 28). The unscaled $\beta$ value for 3p orbital of Na (1.49) is close to that of Ne (1.45$^{29}$) isoelectronic with Na$^+$, justifying our choice of $\beta$ of neutral atoms for use with ions.

26 J.-J. Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters (AT&T Bell Laboratories, Murray Hill, 1993).