Supporting information for: Solvation shell resolved THz spectra of simple aqua ions – distinct distance- and frequency-dependent contributions of solvation shells

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Computational Methods

The DFT-based AIMD simulations¹ were carried out using the CP2K package.^{2,3} We employed the PBE functional,⁴ a TZV2P basis set for atomic orbitals,² and a 600 Ry cutoff for the auxiliary plane wave expansion of the density. The core electrons $(1s^2 \text{ for Na}^+, 1s^22s^22p^6)$ for Cl⁻) were represented by dual-space norm-conserving pseudo potentials.⁵ The systems consisted of 64 H₂O molecules and a single ion. Periodic boundary conditions were applied and each system was contained in a cubic supercell with volume set to reproduce the density of H_2O at 298 K (0.997 kg/m³) combined with the ion's standard partial molar volume in water $(V^{\infty}(\text{Na}^+) = -6.62 \text{ cm}^3/\text{mol}), V^{\infty}(\text{Cl}^-) = 23.24 \text{ cm}^3/\text{mol}),^6$ thus L = 12.41 and 12.51 Å for Na⁺ and Cl⁻, respectively. The systems have been equilibrated for 15 ps at an elevated temperature of 400 K in the canonical (NVT) ensemble using massive Nosé-Hoover chain thermostatting.¹ This choice of the target temperature was demonstrated previously to provide good agreement for the PBE functional with the ambient temperature experimental data for bulk liquid water.⁷ After the equilibration period, 32 statistically independent initial conditions were sampled every 2-3 ps from a further NVT simulation to initialize microcanonical (NVE) trajectories of 20 ps length using a time step of 0.5 fs. During the latter runs the centers of maximally localized Wannier functions (MLWFs)⁸ were computed in an on-the-fly manner every 2 fs and molecular dipole moments were constructed using the centers of these functions. The distance-dependent absorption coefficient was calculated from eqn (S15) using the sharpness parameter D = 0.25 Å. To obtain radially-resolved IR spectra and a correspondingly generalized VDOS, gVDOS, the local dipole and velocity densities according to eqns (S5) and (S10) were computed on a cubic grid with a spacing of 0.539 Å for Na⁺(aq) and 0.544 Å for Cl⁻(aq) $(23 \times 23 \times 23 \text{ grid points})$ using a regularization parameter $\sigma = 0.4$ Å. All analyzed observables have been averaged over the 32 independent NVE trajectories yielding canonical averages.

Radial distribution functions

In the main text, we briefly mention the static structure of the hydration shells of Na⁺ and Cl⁻, as revealed by radial distribution functions. We note in passing that we expect these analyses to be exceptionally well converged in view of the exhaustive sampling of initial conditions required to generate distance-resolved IR spectra. To visualize the structure of the ionic hydration shells, we present here $g_{\rm XO}(r)$ and $g_{\rm XH}(r)$ RDFs for the studied ions in Fig. S1. The most relevant parameters of the RDFs are gathered in Table S1. Our data



Figure S1: Radial distribution functions g(r) (solid lines, left axis) and their running integration numbers n(r) (dashed lines, right axis) for ion-water oxygen (bottom) and ion-water hydrogen (top) pairs for Na⁺ (red) and Cl⁻ (green).

compare favourably with the most recent experimental and AIMD studies, as mentioned in the main text

the main text.

Table S1: Location of the first maxima of the radial distribution functions and normalized integration of the corresponding first peaks up to their first minima (first shell coordination numbers) of $Na^+(aq)$ and $Cl^-(aq)$ as indicated.

Ion	$R_{ m XO}^{ m max}/{ m \AA}$	$n_{\rm XO}^{\rm I}$	$R_{ m XH}^{ m max}/{ m \AA}$	$n_{\rm XH}^{\rm I}$
Na^+	2.40	5.3	2.98	14.7
Cl^-	3.12	5.7	2.88	5.2

To further investigate the relative statistical weight of differently coordinated ion complexes in our simulations, we present in Fig. S2 a histogram of the X–O integer coordination number for the two ions, defined as the number of water oxygens up to the distance of the first minimum in the corresponding RDF, $g_{XO}(r)$. While numerous force field based MD



Figure S2: Integer coordination number (CN) distributions calculated by counting the number of water oxygen atoms up to the first minimum in $g_{\rm XO}(r)$ for Na⁺ (red) and Cl⁻ (green) according to the data shown in Fig. S1.

simulations predicted a hexahydrated sodium cation in aqueous solutions (see Ref. 9 for a review) – thus contradicting experimental findings – it was noted early on that the dominant CN value for Na⁺ is five according to electronic structure based AIMD simulations, $^{9-13}$ as also found here, where CN = 5 occurs in about 50% of the configurations. The preferred arrangement of this complex is close to square pyramidal in the present simulations. For the chloride anion, the hydration sphere appears to be more fluxional since it features penta-and hexahydrated complexes with approximately equal share of CN =5 and 6 together with a wide spread of possible CNs down to CN = 3 and up to 8; the histogram itself is in perfect agreement with previously published ones.^{12,14} A similar coordination mechanism has been recently found for F⁻(aq),¹⁵ where CNs of four and five are most preferred in turn.

Dipole moment distributions

In the main text, we stress the vastly different induced dipole moments of the monatomic ions once they become aqua ions in solution, $Na^+(aq)$ and $Cl^-(aq)$, that prove to be crucial to understand the pronounced high-frequency correlations for $Cl^-(aq)$ in both radially-resolved and distance-dependent IR spectra, which are completely absent in the essentially nonpolarizable $Na^+(aq)$ case. This mirrors the findings in the case of $Li^+(aq)$ and $F^-(aq)$ as recently studied by us.¹⁵ Here, we illustrate our concepts further by presenting distribution functions of the molecular dipole moments for water molecules and both ions in Fig. S3.



Figure S3: Normalized distribution functions of the molecular dipole moments of water molecules in the first solvation shell of Na^+ (red) and Cl^- (green) in comparison to bulk water (black). Inset: Normalized distribution functions of the induced dipole moments of the ions in aqueous solution measured with respect to their center-of-mass using the same color code. The extremely narrow distribution for Na^+ was scaled by a factor of 0.03 to facilitate comparison.

The polarization of the solvent by the ions' electric field lowers the molecular dipole moments of the first solvation shell water molecules in both cases to $\langle \mu \rangle = 2.90$ D for Na⁺(aq) and 2.98 D for Cl⁻(aq), with respect to the corresponding bulk value, $\langle \mu \rangle = 3.04$ D, as obtained using the same simulation setup.¹⁵ The standard statistical error bars of the mean values are estimated to be only about ±0.01 D, while the widths of the essentially Gaussian distributions, as measured by their standard deviation, are ±0.23 D for bulk water and ±0.21 D for first solvation shells of both ions. The lowering of the molecular dipole moments of the first shell water molecules is accompanied by no substantial changes in the widths of their distributions compared to bulk water molecules. These findings are also consistent with earlier reports,^{11,16,17} but recall the exceptional statistical quality of the present data.

The explicit representation of the ions' electronic structure in our AIMD simulations allows us also to estimate the induced dipole moment of the ions in the liquid state (see inset in Fig. S3). We find $\langle \mu_{ion} \rangle$ equal to 0.77 D for Cl⁻(aq), which is consistent with the previous estimate of 0.82 D from AIMD simulations.¹⁶ On the other hand, the Na⁺(aq) cation behaves, not unexpectedly, like an almost nonpolarizable point charge in our simulations. The magnitude of the induced dipole moment never exceeds 0.07 D and the average value is 0.023 D as seen by the (scaled down and extremely narrow) spike close to the origin in Fig. S3. As already mentioned in the main text, the latter finding is especially important considering that the entire $2s^22p^6$ electron shell of Na⁺ is represented explicitly in our AIMD simulations, i.e., we employ in this work a quite hard pseudopotential only for the $1s^2$ shell.

Spatial decomposition of infrared spectra

Here, we review for the convenience of the reader of this Communication the detailed spectra decomposition procedure that leads to distance-dependent and radially-resolved spectra, as presented in Figs. 1, 2, and 4 in the main text. The derivation for solute-solvent systems is based on the recently published paper,¹⁵ which in turn generalizes the methodology originally employed for describing IR absorption in bulk liquid water, both in the radially-resolved⁷ and in the fully three-dimensional picture.¹⁸

The isotropic IR absorption coefficient per unit length is obtained in linear response theory from the Fourier transform of the (classical) total dipole moment of the system M(t). However, since in a charged system the dipole moment depends on the arbitrarily chosen origin of the coordinate system, in this work we use exclusively the dipole moment time derivative, $\dot{M}(t)$, which can also be identified as the total charge current, so that the linear absorption coefficient is calculated as

$$\alpha(\omega) = F(\omega) \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \dot{\boldsymbol{M}}(0) \dot{\boldsymbol{M}}(t) \rangle .$$
(S1)

In order to satisfy the detailed balance condition obeyed by the exact quantum correlation function, eqn (S1) needs to be asymmetrized, which is done by multiplying it using a suitable frequency-dependent prefactor $F(\omega)$, which is often denoted as the "quantum correction factor" (QCF) in the literature. The so-called "harmonic QCF",

$$F(\omega) = \frac{1}{n(\omega)} \frac{1}{4\pi\epsilon_0} \frac{2\pi\beta}{3Vc} , \qquad (S2)$$

has been demonstrated to work especially well for the typical anharmonic vibrational potentials describing H-bonded systems and has found a sound theoretical justification in addition;¹⁹ note that this does not impose the harmonic approximation when computing IR spectra and that the same harmonic QCF has been applied without any adjustment to all reported IR spectra including the decomposed ones. In eqn (S2) the system has volume V, the canonical thermal average $\langle \cdots \rangle$ is evaluated at temperature T, $\beta = 1/k_{\rm B}T$, $n(\omega)$ is the refractive index of the sample, and other symbols carry their usual meanings.

The total dipole moment of a system composed of interacting molecules can be decomposed rigorously into a sum of effective (molecular) dipole moments, ${}^{20-22} \mathbf{M}(t) = \sum_{I=1}^{N} \boldsymbol{\mu}_{I}(t)$, calculated using the centers of the maximally localized Wannier functions (MLWFs).⁸ However, since the MLWF centers are discretely sampled along the trajectory their exact velocities are unavailable, which necessitates the use of finite differences for all degrees of freedom to describe the dipole moment time evolution as $\dot{\boldsymbol{\mu}} \approx \delta \boldsymbol{\mu}/\delta t$, where δt is the time step of the dipole trajectory. To recover the exact results the $F(\omega)$ prefactor in eqn (S2) in all respective Fourier transforms is multiplied by an additional $\operatorname{sinc}^{-2}(\frac{\omega \delta t}{2})$ factor to account for time discretization (vide infra). For a single ion in liquid water, we may decompose the total charge current as follows

$$\dot{\boldsymbol{M}}(t) = \dot{\boldsymbol{\mu}}_{\text{ion}}(t) + \dot{\boldsymbol{\mu}}_{\text{wat}}(t) = \dot{\boldsymbol{\mu}}_{\text{ion}}(t) + \sum_{I}^{\text{solvent}} \dot{\boldsymbol{\mu}}_{I}(t) , \qquad (S3)$$

where $\dot{\boldsymbol{\mu}}_{I}(t)$ is the dipole moment derivative of the *I*th water molecule in solution at time t. This approach allows for the decomposition of the time correlation function (TCF) of the total charge current, $C_{\rm MM}(t) = \langle \dot{\boldsymbol{M}}(0)\dot{\boldsymbol{M}}(t)\rangle$, into auto- and cross-correlations of the ion/water contributions

$$C_{\rm MM}(t) = C_{\rm ii}(t) + C_{\rm ww}(t) + C_{\rm iw}(t)$$
$$= \langle \dot{\boldsymbol{\mu}}_{\rm ion}(0) \dot{\boldsymbol{\mu}}_{\rm ion}(t) \rangle + \langle \dot{\boldsymbol{\mu}}_{\rm wat}(0) \dot{\boldsymbol{\mu}}_{\rm wat}(t) \rangle + \langle \dot{\boldsymbol{\mu}}_{\rm ion}(0) \dot{\boldsymbol{\mu}}_{\rm wat}(0) \rangle + \langle \dot{\boldsymbol{\mu}}_{\rm wat}(0) \dot{\boldsymbol{\mu}}_{\rm ion}(t) \rangle , \quad (S4)$$

that help to identify the respective contributions to the IR spectrum.^{23,24} The solute and solvent component spectra, $\alpha_{ion}(\omega)$ and $\alpha_{wat}(\omega)$, can be obtained by separate Fourier transforms of the two initial terms in eqn (S4), see panel (e) in Fig. 4 (main text) for an example of $\alpha_{ion}(\omega)$ spectra.

As a significant generalization of this long-established approach, we have recently proposed⁷ (see Ref. 18 for generalization) to decompose the total dipole moment (or its time derivative) by defining a smooth local current density of the form

$$\boldsymbol{j}(t,\boldsymbol{r}) = \sum_{I=1}^{N} \dot{\boldsymbol{\mu}}_{I}(t) \frac{1}{(2\pi\sigma^{2})^{3/2}} \exp\left[-\frac{(\boldsymbol{R}_{I}(t)-\boldsymbol{r})^{2}}{2\sigma^{2}}\right] , \qquad (S5)$$

where $\mathbf{R}_{I}(t)$ is the center-of-mass of the *I*th molecule, the regularization parameter σ controls the Gaussian smearing of the current density, and the decomposition is performed on a regular cubic grid \mathbf{r} . Note that the total charge current is recovered from $\dot{\mathbf{M}}(t) = \int_{V} d\mathbf{r} \, \mathbf{j}(t, \mathbf{r})$ integration. Here, we exploit the two-component nature of the studied systems to introduce an ion-centered TCF,

$$C_{\mu j}(t, \boldsymbol{r}) = \langle \dot{\boldsymbol{\mu}}_{\text{ion}}(0) \boldsymbol{j}(t, \boldsymbol{r}) \rangle = 4\pi r^2 \langle \dot{\boldsymbol{\mu}}_{\text{ion}}(0) \boldsymbol{j}(t, r) \rangle = 4\pi r^2 C_{\mu j}^{\text{rad}}(t, r) , \qquad (S6)$$

thus choosing the single solute molecule as a natural reference point. The angular averaging in eqn (S6) comes from the longtime isotropic nature of the homogeneous liquid systems as viewed from the perspective of the solute. Fourier transforming the current-current density TCF,

$$\alpha_{\mathbf{x}}(\omega) = F(\omega) \int_0^\infty dr \int_{-\infty}^\infty dt e^{-i\omega t} 4\pi r^2 C_{\mu j}^{\mathrm{rad}}(t, r) = \int_0^\infty dr \,\alpha_{\mathbf{x}}(\omega, r) \,, \tag{S7}$$

we arrive finally at the radially-resolved IR spectrum of the system, $\alpha_{\mathsf{x}}(\omega, r)$.

The significance of the absorption coefficient defined above lies in its ability to disentangle the spectra at each frequency ω in terms of radially dependent contributions around the solute, i.e., in terms of solvation-shell-resolved contributions to the total IR spectrum. However, in contrast to the previous approach for one-component systems,⁷ what is recovered in the final integration in eqn (S7) is not the total IR spectrum $\alpha(\omega)$ from eqn (S1), but rather a *cross*-correlation spectrum between the solute and the total charge current,

$$\alpha_{\mathbf{x}}(\omega) = F(\omega) \int_{-\infty}^{\infty} dt \mathrm{e}^{-i\omega t} \langle \dot{\boldsymbol{\mu}}_{\mathrm{ion}}(0) \dot{\boldsymbol{M}}(t) \rangle .$$
(S8)

In analogy to the radially-resolved versions of the IR spectrum, we also introduced⁷ a generalized version (gVDOS) of the usual vibrational density of states (VDOS)

$$I(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \boldsymbol{u}_i(0) \boldsymbol{u}_i(t) \rangle , \qquad (S9)$$

where $\boldsymbol{u}_i(t) = \sqrt{m_i} \boldsymbol{v}_i(t)$ is the mass-weighted velocity of the *i*th atom and the TCF includes

averaging over all atoms. We now define the local velocity density as

$$\boldsymbol{\rho}_{u}(t, \boldsymbol{r}) = \sum_{i=1}^{N_{\text{at}}} \boldsymbol{u}_{i}(t) \frac{1}{\left(2\pi\sigma^{2}\right)^{3/2}} \exp\left[-\frac{\left(\boldsymbol{r}_{i}(t) - \boldsymbol{r}\right)^{2}}{2\sigma^{2}}\right]$$
(S10)

In analogy to eqn (S6) we define a similar TCF (again using the ion as natural reference point),

$$C_{u\rho}(t,\boldsymbol{r}) = \langle \boldsymbol{u}_{\rm ion}(0)\boldsymbol{\rho}_u(t,\boldsymbol{r})\rangle = 4\pi r^2 \langle \boldsymbol{u}_{\rm ion}(0)\boldsymbol{\rho}_u(t,r)\rangle = 4\pi r^2 C_{u\rho}^{\rm rad}(t,r) , \qquad (S11)$$

and after Fourier transforming we obtain the radially-resolved function $I_{\mathsf{x}}(\omega, r)$,

$$I_{\mathsf{x}}(\omega) = \int_0^\infty dr \int_{-\infty}^\infty dt \mathrm{e}^{-i\omega t} 4\pi r^2 C_{u\rho}^{\mathrm{rad}}(t,r) = \int_0^\infty dr \ I_{\mathsf{x}}(\omega,r) \ . \tag{S12}$$

Also here the obtained spectrum is the "cross" rather than the total variant, so that

$$I_{\mathbf{x}}(\omega) = \int_{-\infty}^{\infty} dt \mathrm{e}^{-i\omega t} \langle \boldsymbol{u}_{\mathrm{ion}}(0) \sum_{i=1}^{N_{\mathrm{at}}} \boldsymbol{u}_{i}(t) \rangle .$$
(S13)

Complementary to $\alpha_{\mathsf{x}}(\omega, r)$, the $I_{\mathsf{x}}(\omega, r)$ spectrum reveals correlations in particle motion rather than dipolar ones. However, in contrast to the IR absorption there is no "global" counterpart here, as the usual definition of VDOS by means of eqn (S9) does not include cross-correlations of particle velocities.

As yet another way of spatially disentangling the vibrational spectrum, the distancedependent absorption coefficient⁷ offers a detailed picture of how the solvation environment induces characteristic modulations of the IR absorbance around the solute. For the present purpose, it is based on auto-correlating the dipole moment derivative within a finite spherical region around an ion,

$$\dot{\boldsymbol{\mu}}_{\text{ion}}^{\text{P}}(t) = \mathcal{N}_{\text{ion}}^{\text{P}}(t) \left(\dot{\boldsymbol{\mu}}_{\text{ion}}(t) + \sum_{I}^{\text{solvent}} P_{\text{ion},I}(t) \dot{\boldsymbol{\mu}}_{I}(t) \right) , \qquad (S14)$$

where the contributing solvent molecules are selected using Fermi's cutoff function, $P_{\text{ion},I}(t) = 1/\{1 + \exp[(R_{\text{ion},I}(t) - R_0)/D]\}$, controlled by cutoff radius R_0 and sharpness D. To properly account for the (fractional) number of the neighboring solvent molecules I, the distance-dependent dipole moment velocity is normalized with the $\mathcal{N}_{\text{ion}}^{\text{P}}(t) = [1 + \sum_{I} P_{\text{ion},I}^2(t)]^{-1/2}$ factor. Based on this projection of the charge current of the system, the distance-dependent absorption coefficient of the ion-centered region is defined as

$$\alpha_{\rm ion}^{\rm P}(\omega, R_0) = F(\omega) \int dt e^{-i\omega t} \langle \dot{\boldsymbol{\mu}}_{\rm ion}^{\rm P}(0) \dot{\boldsymbol{\mu}}_{\rm ion}^{\rm P}(t) \rangle .$$
(S15)

note that the transition at R_0 is ensured to be continuous with respect to the (fractional) number of solvent molecules by applying the smooth Fermi cutoff function. Moreover, no dangling OH bonds are produced at the boundary of the sphere (and thus no free OH stretching vibrations are introduced by our procedure) since the projector $P_{\text{ion},I}(t)$ acts according to eqn (S14) on the effective molecular dipole (velocities) of the water molecules, $\dot{\boldsymbol{\mu}}_{I}(t)$, and not on the individual atoms and Wannier centers that constitute these molecules. Therefore, we are not artificially carving out from the simulation box a real cluster consisting of a certain integer number of water molecules (which would naturally leave some free OH bonds on its surface), but we rather project out of the periodic bulk environment an embedded cluster with a smooth boundary which contains fractional water molecules in terms of their dipole moment contributions.

The significance of the $\alpha_{ion}^{P}(\omega, R_0)$ spectrum is best revealed by considering the limiting cases. For $R_0 \to 0$ the distance-dependent spectrum and the $\alpha_{ion}(\omega)$ spectrum are identical, as $\dot{\boldsymbol{\mu}}_{ion}^{P}(t) \simeq \dot{\boldsymbol{\mu}}_{ion}(t)$ in this limit. However, in contrast to the radially-resolved IR spectrum that only recovers the cross-correlation spectrum from eqn (S8) in the large distance limit, the distance-dependent dipole moment velocity has a limiting behavior $\dot{\boldsymbol{\mu}}_{ion}^{P}(t) \to \dot{\boldsymbol{M}}(t)/\sqrt{N}$, where N is the number of molecules in the system, as easily inferred from eqn (S14). Therefore, the total IR absorption spectrum from eqn (S1) is simply recovered by multiplication, $\alpha(\omega) = N\alpha_{\rm ion}^{\rm P}(\omega, R_0 \to \infty)$. Most interesting is of course the intermediate regime, where $\alpha_{\rm ion}^{\rm P}(\omega, R_0)$ probes the distinct responses of successive hydration shells of the ion.

The relation between the continuous time derivative and its finite difference estimate

The time derivative of the dipole moment (either total \boldsymbol{M} or molecular $\boldsymbol{\mu}$) is in our approximation not a genuine time derivative $(\dot{\boldsymbol{M}} \text{ or } \dot{\boldsymbol{\mu}})$, but rather a finite difference estimate ($\delta \boldsymbol{M}$ or $\delta \boldsymbol{\mu}$), where $\delta \boldsymbol{M} = (\boldsymbol{M}(t + \delta t) - \boldsymbol{M}(t))/\delta t$. This is a direct consequence of the fact that velocities for Wannier functions' centers are unavailable in the iterative scheme and must be approximated by taking finite differences of their positions at times $t + \delta t$ and t. Below we present a detailed derivation of the respective correction factor for an autocorrelation function of a finite difference property.

$$\begin{split} I_{\mathbf{M}}(\omega) &= \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} \\ \delta \mathbf{M}(t) &= (\mathbf{M}(t+\delta t) - \mathbf{M}(t))/\delta t \\ I_{\delta \mathbf{M}}(\omega) &= \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \delta \mathbf{M}(t+\tau) \delta \mathbf{M}(t) \rangle_{t} \\ &= \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\delta t+\tau)\mathbf{M}(t+\delta t) \rangle_{t} - \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\delta t+\tau)\mathbf{M}(t) \rangle_{t} \\ &- \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t+\delta t) \rangle_{t} + \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} \\ &= \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} - \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} \\ &= \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} - \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}(\tau+\delta t) \; \mathrm{e}^{-i\omega(\tau+\delta t)} \; \mathrm{e}^{i\omega\delta t} \; \langle \mathbf{M}(t+(\tau+\delta t))\mathbf{M}(t) \rangle_{t} \\ &- \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}(\tau-\delta t) \; \mathrm{e}^{-i\omega(\tau-\delta t)} \; \mathrm{e}^{-i\omega\delta t} \; \langle \mathbf{M}(t+(\tau-\delta t))\mathbf{M}(t) \rangle_{t} + \frac{1}{\delta t^{2}} \int_{-\infty}^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-i\omega\tau} \; \langle \mathbf{M}(t+\tau)\mathbf{M}(t) \rangle_{t} \\ &= \frac{1}{\delta t^{2}} (I_{\mathbf{M}}(\omega) - \mathrm{e}^{i\omega\delta t}I_{\mathbf{M}}(\omega) - \mathrm{e}^{-i\omega\delta t}I_{\mathbf{M}}(\omega) + I_{\mathbf{M}}(\omega)) \\ &= \frac{1}{\delta t^{2}} (2 - \mathrm{e}^{i\omega\delta t} - \mathrm{e}^{-i\omega\delta t}) \; I_{\mathbf{M}}(\omega) = \frac{2 - 2\cos(\omega\delta t)}{\delta t^{2}} I_{\mathbf{M}}(\omega) \\ &I_{\delta \mathbf{M}}(\omega) = \left(\frac{2}{\delta t} \sin \frac{\omega\delta t}{2}\right)^{2} \; I_{\mathbf{M}}(\omega) \end{aligned}$$

Numerical Kramers-Kronig transforms

The complex dielectric function, $\epsilon_r(\omega) = \epsilon'_r(\omega) + i\epsilon''_r(\omega)$, obeys the Kramers-Kronig relation

$$\epsilon'_r(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon''_r(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(S16)

for $\omega \ge 0$ and P denoting the principal value of the integral. The complex dielectric function is also connected to the complex refractive index, $\hat{n}(\omega) = n(\omega) + ik(\omega)$, via $\hat{n}^2(\omega) = \epsilon_r(\omega)\mu_r(\omega)$.

Assuming that the relative magnetic permeability, $\mu_r(\omega)$, is unity for most dielectrics, and connecting imaginary refractive index and linear absorption coefficient via $k(\omega) = \frac{c}{2\omega}\alpha(\omega)$, we can relate respective components of the complex dielectric function and the complex refractive index, so that

$$\epsilon'_{r}(\omega) = n^{2}(\omega) - \frac{c^{2}}{4\omega^{2}}\alpha^{2}(\omega) ,$$

$$\epsilon''_{r}(\omega) = \frac{c}{\omega}\alpha(\omega)n(\omega) = \frac{c}{\omega}I_{\alpha}(\omega) , \qquad (S17)$$

where $I_{\alpha}(\omega)$ is the (entangled) spectrum typically derived from the total dipole moment evolution during an MD trajectory, see above.

The integral in eqn (S16) must be split into three ranges due to the lack of electronic excitation spectrum in our AIMD simulation:

 Up to the maximal frequency ω_{max} ≈ 8340 cm⁻¹, as determined by the time resolution of our AIMD simulation, we can calculate the integral directly, avoiding the pole at ω = ω' by separating the integrand into two functions,

$$P \int_{0}^{\omega_{\max}} \frac{\omega' \epsilon_{r}''(\omega')}{\omega'^{2} - \omega^{2}} d\omega' = P \int_{0}^{\omega_{\max}} \frac{\epsilon_{r}''(\omega)}{2(\omega' - \omega)} d\omega' + \int_{0}^{\omega_{\max}} \frac{\frac{\omega' \epsilon_{r}''(\omega')}{\omega' + \omega} - \frac{\epsilon_{r}''(\omega)}{2}}{\omega' - \omega} d\omega' .$$
(S18)

Here, the first integral is just $\frac{\epsilon_r''(\omega)}{2} \ln \frac{\omega_{\max} - \omega}{\omega}$ and the second integral is easily evaluated numerically, since

$$\lim_{\omega'\to\omega} \frac{\frac{\omega'\epsilon_r''(\omega')}{\omega'+\omega} - \frac{\epsilon_r''(\omega)}{2}}{\omega'-\omega} = \frac{\epsilon_r''(\omega)}{4\omega} + \frac{1}{2}\frac{d\epsilon_r''(\omega)}{d\omega} .$$
 (S19)

2. For $\omega_{\text{max}} < \omega < \omega_{\text{el}}$, where ω_{el} is the lowest electronic excitation frequency, the imaginary dielectric function $\epsilon_r''(\omega') \to 0$ and the respective integral is also close to 0. 3. For $\omega > \omega_{\rm el}$ we have $\omega' \gg \omega$ and therefore $\omega'^2 - \omega^2 \approx \omega'^2$. Thus, this range of the integral only contributes a nearly constant offset,

$$\frac{2}{\pi} \int_{\omega_{\text{max}}}^{\infty} \frac{\epsilon_r''(\omega')}{\omega'} d\omega' = \text{const} \approx n_{\text{gap}}^2 - 1 , \qquad (S20)$$

where n_{gap} is the nearly constant value of the refractive index in the optical gap, $\omega_{\text{max}} < \omega < \omega_{\text{el}}$, which for water and solutions of substances non-absorbing in the visible range may be approximated by the experimentally measured sodium D–line value at 589 nm, n_{D} . This value is determined here from the experimental value for a 0.8 molal NaCl solution (approximately our simulated concentration), $n_{\text{D}} = 1.34$.²⁵

Once the real part of the dielectric function is determined, we can revert to eqn (S17) to obtain $\alpha(\omega)$ and $n(\omega)$ separately as

$$\alpha(\omega) = \frac{\omega}{c} \sqrt{2\left(\sqrt{\epsilon_r'^2(\omega) + \epsilon_r''^2(\omega)} - \epsilon_r'(\omega)\right)},$$

$$n(\omega) = \sqrt{\frac{\epsilon_r'(\omega) + \sqrt{\epsilon_r'^2(\omega) + \epsilon_r''^2(\omega)}}{2}}.$$
 (S21)

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