Excess protons revealed in the infrared spectrum of liquid water

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The most common species in liquid water, next to neutral H2O molecules, are the H3O+ and OH− ions. Though they contribute to the infrared (IR) spectrum, they remain hidden within the broad absorption lines of neutral molecules. This severely hinders the interpretation of the spectroscopic data. Using a spectral-weight analysis, here we experimentally resolve the fingerprints of H3O+, DH2O+, HD2O+, and D2O+ ions in the IR spectra of light (H2O), heavy (D2O), and semi-heavy (HDO) water. We calculate the normal vibration modes of these ions, assign them to certain spectral features, and determine the ion concentrations. We find that the fluctuations-born short-living ions with a concentration of about two percent of the content of water molecules, coexist with long-living pH-active ions. We conclude that water is a “two-percent ionic liquid” at least on timescale shorter than picoseconds.

I. INTRODUCTION

The H3O+ and OH− ions drive the charge transfer process and acid-base reactions in aqueous solutions, and serve as intermediates for protonic transport [1–2], as such, they are important species in biology, chemical physics, and electro-chemistry. These two ionic species are characterized by picosecond-scale lifetimes in liquid water [3]. Low-speed methods, such as nuclear magnetic resonance, potentiometry, and conductometry, only provide limited information on water’s microscopic properties while faster techniques, such as pump-probe [4], terahertz [5] and infrared (IR) [6] spectroscopy, are in principle better suited to probe ultra-fast (sub picosecond) dynamics. However, the main difficulty with these latter methods is that the spectral features of these ions are impossible to observe directly as the ionic concentrations are typically much lower than that of the neutral H2O molecules [7]. For that reason detailed studies of molecular dynamics of liquid water heavily rely on numerical simulations [8]. And, despite extensive experimental and theoretical studies, the assignment of the water ions to the actual (observable) spectral features are still crucially missing [9–12], thus precluding the detailed understanding of the ions’ role in the microscopic properties of liquid water.

Femtosecond fluctuations of molecules in water at room temperature lead to spontaneous formation of short-living (SL) ions, H2O+ and OH+ [13]. The formation-recombination pathway of SL ions is inter-molecular, but the ion trajectories are loop-shaped [14]. Random thermal disturbances sometimes break the circle, providing a transfer of the SL ions to the ordinary long-living (LL) pH-active H3O+ and OH− ions [15–16]. Both types, SL and LL ions, are of the same origin, but only the latter are detectable with slow measurement techniques. However, the “instantaneous” concentration of the SL ions is much higher than the LL’s ones [17–19]. The SL ionic concentration of about 1 M was suggested to be responsible for the Deybe relaxation of water (a strong absorption band in the gigahertz range) [19–20], but, because of the short lifetime (3 ps) of these ions, their contribution to the dc conductivity is small [20–21].

Since on time scales shorter than picoseconds, water has a constant chemical composition in terms of ionic and molecular species, both LL and SL ions should contribute to the IR (and higher energy) spectrum. However, the structure of water IR spectrum is such that it cannot be used for the direct identification of the ions’ contributions because of strongly overlapping bands with multiple contributions, as demonstrated in [22]. Moreover, ionic vibrations, which are absent in water vapor [23] and cannot be easily identified in the condensed phase, are entangled with intramolecular oscillations in liquid water [24]. The goal of this paper is to determine the elusive ionic contributions to the water IR spectrum. The replacement of protons (one or several) in the ionic species by deuterons, shifts spectroscopic lines and makes ionic species “visible” in the integral spectrum. The spectral-weight analysis shows that up to picosecond timescales water is composed of a significant amount of short-lived ionic species, influencing the nature of intermolecular interactions.

II. EXPERIMENTAL

Samples of H2O and D2O with purity of 99.9% obtained from Sigma-Aldrich were used in this work. Probes with different molar fractions of deuterium, \( f = D/(H + D) \), were prepared by mixing pure light and heavy water before measurements. The spectra were recorded in transmission mode using a Bruker Vertex 80v spectrometer in the frequency range 600–8000 cm−1. For these measurements, a drop of water was sandwiched between two 3-mm-thick ZnSe windows. ZnSe is perfectly

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suited for such a type of measurements: it is hydrophobic and highly transparent with no absorption lines in the range of interest. There were no spacers between the windows. Instead, we controlled the stabilization of the water layer, measuring the IR spectra every 30 seconds until they were stabilized. The thickness for the light, heavy, and semi-heavy water samples was about 1 μm, slightly varying from sample to sample. The reference spectrum of the windows was recorded separately in advance. In order to eliminate the multiple reflections inside the water layer, the spectra were processed using a five-media model [25] and an algorithm of least-squares minimization [26].

For our study, we intentionally chose the transmission mode (TIR) instead of the attenuated total reflection (ATR) technique [27]. Although the ATR method provides the spectra without any fringes caused by multiple reflections within the water layer, the true absorption spectrum with the absolute values of transmitted intensity is only available in the TIR. As there is a discrepancy between the liquid water spectra obtained by these two methods (see Appendix), for the spectral weight analysis and the calculation of the ion concentrations a directly obtained TIR spectrum was used.

III. RESULTS

![Dynamical conductivity spectra](image)

**FIG. 1.** Experimental spectra of dynamical conductivity \(\sigma(\nu)\) of (A) pure light and pure heavy water, and (B) mixtures of light and heavy water with different molar isotopic fractions \(f\) as indicated. The arrows show two stretching modes above 2000 cm\(^{-1}\), and three bending modes below 2000 cm\(^{-1}\). The thin vertical lines are guides for the eye.

Table I. Frequencies \(\nu\) in cm\(^{-1}\) (upper rows) and integral intensities \(I\) in S·cm\(^{-2}\) (in brackets on lower rows) of the bending and stretching vibrations peaks shown in Fig. 1.

| \(f\) | DOD (cm\(^{-1}\)) | HOD (cm\(^{-1}\)) | HOH (cm\(^{-1}\)) | OD (cm\(^{-1}\)) | OH (cm\(^{-1}\)) |
|------|------------------|------------------|------------------|----------------|---------------|
| 0    | n/a              | n/a              | 1658             | n/a            | 3414          |
|      | (3360)           |                  |                  |                | (29745)       |
| 1/4  | 1217             | 1461             | 1651             | 2510           | 3413          |
|      | (216)            | (789)            | (916)            | (4800)         | (24552)       |
| 1/2  | 1217             | 1457             | 1653             | 2509           | 3410          |
|      | (385)            | (961)            | (509)            | (8913)         | (16822)       |
| 3/4  | 1214             | 1458             | 1651             | 2507           | 3396          |
|      | (735)            | (793)            | (215)            | (13303)        | (10023)       |
| 1    | 1213             | n/a              | n/a              | 2506           | n/a           |
|      | (1554)           |                  |                  | (19351)        |               |

Terms of dynamical conductivity has an important advantage: the integral under a mode in the \(\sigma(\nu)\) curve is directly proportional to the number of charges involved in the absorption mechanism responsible for this mode (e.g., in corresponding vibration or rotation). This allows one to account for the concentration of species that contribute to the certain mode. One can clearly see the two groups of vibrational bands: at 1000-2000 and 2000-4000 cm\(^{-1}\). The central frequencies and integral intensities of these bands are presented in Table I. The right-side portion of the spectrum (frequencies above 2000 cm\(^{-1}\)) contains the O–H and O–D stretching modes, while the left-side portion (below 2000 cm\(^{-1}\)) hosts the H–O–H, D–O–D, and H–O–D bending modes [28]. Obviously, the H–O–D modes appear only in spectra of H\(_2\)O/D\(_2\)O mixtures (see Fig. 1B). All bands are intense, wide, and possess complex internal structures (consist of several Lorentzians). The relative shift of the H\(_2\)O and D\(_2\)O lines well matches the shift of the normal modes of the corresponding harmonic oscillators (see the Appendix for details).

While the spectra of light and heavy water can easily be obtained in an experiment, the “actual” spectrum of HDO cannot be measured directly. In order to pinpoint the HDO modes, the experimental studies suggested to consider spectra of the mixtures as weighted sums of the spectra of light, heavy, and semi-heavy water [29, 30]. For the dynamical conductivity spectra of mixtures \(\sigma_{\text{mix}}(\nu, f)\) with different \(f\), we write:

\[
\sigma_{\text{mix}}(\nu, f) = a\sigma_{\text{D}_2\text{O}}(\nu) + b\sigma_{\text{H}_2\text{O}}(\nu) + c\sigma_{\text{HDO}}(\nu)
\]  (1)

where \(\sigma_{\text{D}_2\text{O}}(\nu)\), \(\sigma_{\text{H}_2\text{O}}(\nu)\), \(\sigma_{\text{HDO}}(\nu)\) are \(f\)-independent spectra, and the coefficients \(a = f^2\), \(b = (1 - f)^2\), and \(c = 2f(1 - f)\), are the probabilities of formation of D\(_2\)O,
H₂O, and HDO, respectively. If only these three species are assumed in a mixture, the HDO spectrum calculated from Eq. (1) should be f-independent, or, in other words, should be the same for all values of the molar fraction f.

![Graph](image)

**FIG. 2.** (A) Spectra of pure HDO calculated from the spectra shown in Fig. 1 using Eq. (1); (B,C) Magnified parts of the HDO spectra near the D−O−D and H−O−H bending modes showing “S-shaped” mismatches (see text). The numbers near the curves correspond to the molar fraction f. In all panels, the spectra for f = 1/2 and f = 1/4 are shifted upwards for clarity. Arrows indicate the areas, where the mismatches of the spectra, S₁ and S₂, occur.

Figure 2 shows spectra of HDO calculated using Eq. (1) from the spectra displayed in Fig. 1. The HDO spectra generally coincide with each other; however, there are very characteristic mismatches (“S-shaped” features) near the D−O−D and H−O−H bands (Fig. 2A). The presence of these S-features suggests either that the measured spectra are not accurate enough or that species other than H₂O, D₂O, and HDO, are present in the mixture. We are inclined to the second scenario for the following reasons. First, we found that in our measurements, the intensities of the mismatches shown in Fig. 2 surely exceed the uncertainty of the TIR measurements and the error of spectra processing (see the Appendix).

Next, very similar S-shape mismatches in the HDO spectra obtained in the same frequency region have been reported earlier [29, 30]. Most importantly, the frequency, and amplitude of the S-features are reproducible and consistently changing with the molar fraction f. Furthermore, the S-feature near the D−O−D bend (Fig. 2B) is mirror-symmetric in shape with respect to the S-feature near the H−O−H bending mode (Fig. 2C). This observation is in contrast to one of the previous studies [29], where both S-features are shown identical; but it is in agreement with a more precise recent study [30], where the similar pattern of the S-features were demonstrated at the analysis of absorption spectrum. Finally, the ratio between the integral intensities of the positive and negative components for the S-feature (see Figs. 2B, C) is 3:1, independently on the mole fraction f. From these points we conclude that the S-features are due to internal species of liquid water that are not taken into account by Eq. (1), as this relation includes only molecular components. Below we argue that short-lived intrinsic ions of water are good candidates for the missing water species and that the density of these ions is relatively high.

**IV. DISCUSSION**

![Diagram](image)

**FIG. 3.** (A) Nine principal water species, present in light and heavy water (groups 1 and 2, respectively) and in their mixtures (all three groups). The rows correspond to neutral molecules (row i) and positively (row ii) and negatively (row iii) charged ions. (B) Percentage of the water species in pure H₂O (red), pure D₂O (blue) and their 1:1 mixture (shaded) according to Table I. (C) Differences in ion concentrations obtained after subtraction of the normalized bars for pure light and heavy water (red and blue) from the ones for the mixtures (shaded), according to Eq. (1). Numbers near zero-lines are mole the fraction f. The data shown in panel (B) correspond to the middle raw in panel (C).
Table II. Percentage of species (neutral molecules and ions) in liquid H$_2$O, D$_2$O and their mixtures. Ions are marked with asterisks.

|   | 0  | 1/4 | 1/2 | 3/4 | 1   |
|---|----|-----|-----|-----|-----|
| f |    |     |     |     |     |
| HDO | 0  | 36.56 | 48.75 | 36.56 | 0   |
| H$_2$O | 97.5 | 54.84 | 24.38 | 6.094 | 0   |
| D$_2$O | 0  | 6.094 | 24.38 | 54.84 | 97.5 |
| H$_2$O* | 1.25 | 0.527 | 0.156 | 0.020 | 0   |
| D$_2$O* | 0  | 0.020 | 0.156 | 0.527 | 1.25 |
| DH$_2$O* | 0  | 0.527 | 0.469 | 0.176 | 0   |
| HD$_2$O* | 0  | 0.176 | 0.469 | 0.527 | 0   |
| OH* | 1.25 | 0.313 | 0.625 | 0.938 | 0   |
| OD* | 0  | 0.938 | 0.625 | 0.313 | 1.25 |

A. Composition of liquid water

Fig. 3A depicts nine principal species - neutral molecules and ions - for mixtures of light and heavy water. The species H$_2$O, H$_3$O*, OH* (group 1) and their deuterated isotopologues D$_2$O, D$_3$O*, OD* (group 2) constitute pure light and heavy water, respectively. The species HDO, HD$_2$O*, DH$_2$O* (group 3) are only present in water mixtures, where they coexist with the six species of the groups 1 and 2. Thus, in addition to the three molecular species (line i of Fig. 3A), a mixture contains also four positively charged ions (line ii) and two negatively charged ions (line iii). The relative proportion of these nine species is determined by the autoionization-recombination events, but it also depends on the molar fraction $f$. Here and below, we do not distinguish the SL ions and LL ions: albeit their lifetimes differ, they are indistinguishable on the short timescales relevant for IR vibrations.

Inasmuch as it is difficult to detect concentration the SL ions in water directly, we rely on studies based on the terahertz absorption measurements [13], as well as on molecular dynamics simulations that take into account the auto-dissociation events in the frame of the semiclassical approach [21]. Both studies conclude that the approximate concentration of the SL ions is about 1 M (or about 2%). In a more recent investigation [19] - based on the analysis of broadband spectrum of water - the concentration of ionic species accounts to 2.5%. Hereinafter we choose this value for our preliminary analysis, and it will be later confirmed by the fit of the experimental data.

Table II lists the calculated percentage of nine principal species (“particles”) of water mixtures for different molar fractions $f$. The concentrations of the particles are obtained by the combinatorial probability of permutation of H and D atoms around the oxygen atom O in the assumption that: (i) the probabilities for formation of the covalent H and D bonds are the same; (ii) the relative percentages of ions and molecular species are identical for all mixtures; (iii) the SL ions concentration is $n_i = 2.5\%$; and (iv) the concentration of positively charged ions is equal to the concentration of negatively charged ions, $n^+ = n^- = n_i/2$ (charge-neutrality). The concentrations of positively charged ions are calculated from the total concentration $n^+$ of positive ions using the following coefficients $(1−f)^3$, $f^3$, $3f(1−f)^2$, and $3f^2(1−f)$ for H$_3$O*, D$_3$O*, DH$_2$O*, and HD$_2$O*, respectively. These coefficients are the probabilities to form these ions from H and D atoms available in the mixtures. Concentrations of negatively charged ions $n^-$, we obtained utilizing $f$ and $(1−f)$ as such probability coefficients for OH* and OD*, respectively.

Figure 3B presents the concentration bars for all 9 possible species in light water ($f = 0$), heavy water ($f = 1$) and their 1:1 mixture ($f = 1/2$). The column bars correspond to the values given in Table II. As long as the total concentrations of positive and negative ions (charges) $n^+$ and $n^-$ are fixed, it is distributed among a larger number of different species (types of ions) in a mixture than in pure H$_2$O or D$_2$O. For example, the population density of OH* of pure light water in the mixture is distributed between OH* and OD*. The same for positively charged species: the asymmetric HD$_2$O* and DH$_2$O* ions, present in the mixtures only, take a part of the total charge density from the symmetric H$_3$O* and D$_3$O* ions (see the differences between the bars for pure H$_2$O or D$_2$O and for the mixtures in Fig. 3B). This effect was unaccounted for in the above IR-spectrum analysis.

If we now apply the normalization coefficients $a$, $b$, and $c$ (same as were used in Eq. (1)) to the column bars of mixture, pure light and pure heavy water, respectively, we equilibrate the concentrations of molecular species only. The bars of ionic species for the pure probes and the mixtures will not coincide, because the relative ratio of the ionic species and the molecular species in the mixture differs from those in the pure light or heavy water. In other words, the normalized bars are subtracted properly for molecular species only, but not for the ionic species.

Figure 3C exhibits the differences obtained after subtraction of the normalized bars for pure light and heavy water from the bars corresponding to the mixtures (for $f = 1/4$, 1/2, and 3/4). As one can see, the H$_2$O and D$_2$O bars are subtracted completely, and all evaluated HDO-concentration columns coincide with each other ($\Delta N = 97.5\%$ everywhere), but the ionic bars differ. The number of H$_3$O* and D$_3$O* ions and the number of HD$_2$O* and DH$_2$O* ions are, respectively, over- and under-estimated. Asymmetric ions are not sub-
tracted because they do not exist in pure light and heavy water, while concentrations of symmetric ions are over-evaluated. The same applies for negatively charged OH* and OD* ions. Their relative concentrations in the mixture differ from those for neutral molecules, which leads to the corresponding residual bars after subtraction.

As the probability of the formation of asymmetric ions is three-times-higher than for symmetric ones, the relative ratio of the concentrations of up-going and down-going residual bars of positively charged ions in Fig. 3C is 3:1 everywhere (compare the bars for H3O* and DH2O*, as well as, D3O* and HD2O* for each probe). The ratio is the same as observed for the positive and negative parts of the experimentally observed S-features in Fig. 2. This, as well as the fact that the intensities of S-features are proportional to the concentration of ionic species, make it possible to identify ions in the spectrum and calculate their concentrations.

### B. Assignment of the S-features

Because the OH*- and OD*-ion vibrations are very close to the O–H and O–D stretching modes, they are hidden within the bands at 2450 and 3400 cm⁻¹ (see Fig. 2A). However, the positively charged ions, D3O*, HD2O*, DH2O*, and H3O* possess vibrational modes, whose frequencies are different, and also from the HDO, H2O, and D2O frequencies. Thus, the concentrations of the positively charged ions in the mixtures can be identified by comparing their IR spectra.

![FIG. 4. (A) Bending oscillations of positively charged ions in mixtures of light and heavy water. Black circles are D atoms, small open circles are H atom, large open circles are O atoms. (B) A harmonic-oscillator model representing these vibrations with the normal modes defined by Eq. (2).](image)

Figure 4 sketches the bending vibrations of positively charged ions, whose frequencies are expected to be close to (but still different from) the bending frequencies of H2O and D2O at 1650 and 1240 cm⁻¹, respectively (see Fig. 1). If we now utilize a simple harmonic-oscillator model with three masses and three springs depicted in Fig. 1, two modes with the following nonzero eigenfrequencies are expected:

\[
\omega_1 = \sqrt{(2k' + k)/m} \quad \text{and} \quad \omega_2 = \sqrt{2k/\mu} \quad (2)
\]

where \(k\) and \(k'\) are the spring constants, \(\mu = 2mM/(2m+M)\) is the effective mass (which is given in Table III for different species of water), \(m\) is the mass of deuteron or proton, and \(M\) is the mass of one oxygen atom (plus the mass of one deuteron or proton in the case of DH2O* and HD2O* ions). The mode with the eigenfrequency \(\omega_2\) corresponds to bending vibrations shown in Fig. 4. The second mode is a stretching vibration and is not relevant for this study. The spring constant \(k'\) (which correspond to the vibrations between the light atoms) is close to zero, while \(k\) (the vibrations between a light atom and heavy oxygen) is equal to 142 ± 4 N/m for both H2O and D2O, as can be defined from the experimental frequencies of H2O and D2O molecules and Eq. (2).

The constant \(k\) is not expected to change much across the isotopologues and from Eq. (2) one should expect that: (i) the heavier ions have lower oscillation frequencies and (ii) D3O* and HD2O* have their vibrational frequencies close to the D2O bending mode, while the frequencies of DH2O* and H3O* are close to the bending mode of H2O. Thus, the spectral fingerprints of the ions illustrated in Fig. 4 are expected to appear in the following order with increasing frequency: H2O*, DH2O*, HD2O*, and D3O*, first two being around 1660 cm⁻¹, while the last two showing up near 1210 cm⁻¹.

Figure 5 shows the experimental spectra of heavy and light water in the vicinity of the D–O–D and H–O–H bending modes. The red curves are the least-square fits with a sum of three Lorentz oscillators: one is for the “parent”, e.g. H2O or D2O molecule, and two are for ions, as indicated. The oscillator parameters for the ions were obtained by performing a simultaneous fitting of the measured spectra and the corresponding S-features from Fig. 3 using the following equations:

|       | \(M\) | \(m\) | \(\mu\) | \(k\) | \(\nu_2\) | \(\nu_2^{\text{exp}}\) |
|-------|-------|-------|-------|------|--------|--------|
| H2O   | 16    | 1     | 1.778 | 145  | 1663   | 1638   |
| D2O   | 16    | 2     | 3.200 | 139  | 1213   | 1204   |
| H3O*  | 17    | 1     | 1.789 | 151  | 1695   | 1714   |
| DH2O* | 18    | 1     | 1.800 | 142  | 1637   | no data |
| HD2O* | 17    | 2     | 3.238 | 142  | 1222   | no data |
| D3O*  | 18    | 2     | 3.273 | 138  | 1195   | 1194   |

\(a\) From Ref. [32].
\(b\) From Ref. [27].
\(c\) From Ref. [28].
FIG. 5. Conductivity spectra of heavy (left) and light (right) water near the D–O–D and H–O–H bending modes. Open circles are the experimental data; red curves are fits with three Lorentz oscillators, one for the parent molecule (D$_2$O or H$_2$O) and two for the contributions from the ionic species (see Table III). The bottom panels show the S-features, obtained via subtraction of the curves with the contributions from the asymmetric ions from the curves without such contributions (see Eqs. (3) and (4)), in comparison with the experimental curves (dots) from Fig. 2.

\[
\Delta \sigma_{S_1} = \left[ \sigma_{H_2O} + \sigma_{D_2O^+} + \sigma_{H_2O^+} (1 - f^3) \right] - \left[ \sigma_{H_2O} + \sigma_{H_2O^+} \right] \quad (3)
\]

\[
\Delta \sigma_{S_2} = \left[ \sigma_{D_2O} + \sigma_{D_2O^+} + \sigma_{D_2O^-} f^3 \right] - \left[ \sigma_{D_2O} + \sigma_{D_2O^+} \right] \quad (4)
\]

where all where \( \sigma_i \)'s are functions of \( \nu \): \( \sigma_i(\nu) = I_i \omega_i^2 \left[ \omega_i^2 + (\nu_{oi} - \nu)^2 \right] \) is Lorentz-oscillator contribution to the dynamical conductivity, with \( I_i \) being its intensity, \( \omega_i \) its half-width, \( \nu_{oi} \) the oscillator central frequency, and \( f \) is the D$_2$O molar fraction in the water mixture, as already defined. The fit parameters are in Table IV. One can see a perfect agreement between the model and the experimental data. Thus, the mismatches in the subtracted HDO spectra are assigned to the SL ionic species that are parts of the IR spectra of light and heavy water, as well as their mixtures.

S-features in the subtracted spectra of HDO were already reported in [30], where spectral data were analyzed in terms of absorption \( \alpha = 4 \pi \sigma(\nu)/n(\nu)c \), where \( c \) is a speed of light, \( n(\nu) \) is the frequency dependent refractive index; unfortunately it cannot reflect the true concentration of ionic species. Nevertheless, the residues in the HDO spectra are quite similar to ours, indirectly confirming our results. The authors interpret the residues in terms of hydrogen bonding, considering the perturbation of the intramolecular vibrations caused by surroundings, as they assumed that molecular species (H$_2$O, D$_2$O, and HDO) oscillation frequencies change by the neighboring atoms that provide hydrogen or deuterium bonds [30]. In spite of their very careful spectral analysis, this physical interpretation lacks clarity mainly because the expected concentrations of perturbed molecules are too high compared to our observations values (Fig. 5). For example, in the 1:1 mixture of light and heavy water, one expects that half of the bonds with neighboring molecules are formed by deuterons, while the residuals are too small to be explained in this way. We believe our approach to the interpretation of the IR spectra of D$_2$O/H$_2$O mixtures by introduction of the ionic species is more suitable.

### C. Concentration of ions

Having understood the origin of the discrepancy of the “pure” HDO spectra obtained at different molar fractions \( f \), we can calculate the concentration of ionic species in water from their S-features. The spectral weight \( S \) of a Lorentz oscillator is related to the density of charges involved in the absorption process [33]:

\[
S_i = \frac{\int_0^\infty \sigma(\omega')d\omega'}{\pi} = \frac{n_i q_i^2}{2 \mu_i} \quad (5)
\]

where \( \mu_i \), \( q_i \) and \( n_i \) are the effective mass, charge, and concentration of the conducting species of the \( i \)-th kind. Taking into account the effective masses and the parameters of Lorentzians obtained above, one can calculate the concentrations of the corresponding water species. The results are summarized in Table IV. The concentrations obtained are in good agreement with the expected...
percentage for the different species in liquid water presented in Table II. Thus, we have shown that the subtraction residuals shown in Figs. 2B, C correspond to the unaccounted ionic species of H$_2$O$^*$, DH$_2$O$^*$, HD$_2$O$^*$, and D$_3$O$^*$.

V. CONCLUSION

We have studied the infrared spectra of the H$_2$O, D$_2$O, and their mixtures in the direct transmission mode to uncover the hidden IR vibrations of water’s ionic species. Our study reveals that the intramolecular vibrational dynamics observed in the IR spectrum of water is not confined to the oscillatory motion of molecular species only. The presence of the residues on the spectrum of “pure” HDO, obtained from the mixtures with different mole fractions of light and heavy water, clearly shows that absorption of IR waves by water is partially defined by the dynamics of ionic species, whose concentration (at least at short times < 0.1 ps the low frequency limit of TIR) is about 2% of the total number of molecules in liquid water. In order to bring this result in accord with pH concept, we suggest that fluctuation-driven short-living ions coexist with conventional long-living pH-active ions at short times of observation corresponding to the IR frequency range. The detected ionic species are important for water related processes, e.g. solvation, dissolution, osmosis, cavitation, radiolysis, which take place on short space (nanometer) and time (sub-picosecond) scales.[54][55]. We expect the ionic species related transfer anomalies, which are important for biological, physical-chemical, and electrochemical systems. These space-time intervals are suitable for ab-initio approaches, and molecular dynamics simulations are highly welcome.

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FIG. 6. Sets of absorption spectra of water in infrared region squeezed between two ZnSe windows in infrared frequency region: (A) pure H₂O, (B) pure D₂O. The time interval between the measurements is 30 seconds. The parameter $d_{eq}$ is the effective water layer thickness at equilibrium.
FIG. 7. Same as in Fig. 6 for light and heavy water mixtures: (A) 75% H$_2$O and 25% D$_2$O, (B) 50% H$_2$O and 50% D$_2$O, (C) 25% D$_2$O and 75% H$_2$O.
FIG. 8. Spectra of optically polished ZnSe windows used for the measurements: (A) separately; (B) two windows together. The thickness of each window is $3.0 \pm 0.1$ mm.
FIG. 9. Molar fractions of the components of light and heavy water mixtures as a function of molar isotopic fraction \( f \). The curves are obtained with the equation \( K = [\text{HDO}]^2/([\text{H}_2\text{O}][\text{D}_2\text{O}]) \approx 3.85 \) and the formulas given in the legend. Numbers near the curves are for \( f = 1/4, 1/2, 3/4 \) - the molar fractions of the mixtures, whose spectra are shown in Fig. 7.

FIG. 10. Partial integrals of spectra shown in Figs. 1 and 2, in the main text.
FIG. 11. Comparison of ATR (attenuated total reflection - black) and TIR (direct transmission - blue) spectra by relative subtraction (red). One expects that the difference should be a pure Airy-like function, but the characteristic deviations are observed near the stretching and bending modes. ATR data are from the Ref. [30] of the manuscript.