

Pure Molecular Beam of Water Dimer

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Spatial separation of water dimers from water monomers and larger water-clusters through the electric deflector is presented. A beam of water dimers with 93 % purity and a rotational temperature of 1.5 K was obtained. Following strong-field ionization using a 35 fs laser pulse with a wavelength centered around 800 nm and a peak intensity of 10^{14} W/cm² we observed proton transfer and 46 % of ionized water dimers broke apart into hydronium ions H₃O⁺ and neutral OH.

INTRODUCTION

Hydrogen bonding between water molecules plays an important role in aqueous systems, e. g., for biomolecules that are surrounded by solvents. It is responsible for the unique properties of water, such as its high boiling point [1]. While hydrogen bonds have been studied extensively in many different molecular systems [2–8], one of the most important models remains the water dimer, somehow the smallest drop of water. Numerous studies have been conducted on this benchmark system and its structure with a single hydrogen bond is well known [9–12].

Water molecules and water-clusters have been studied using various techniques to describe dynamics such as proton motion [13] or chemical processes, e. g., reactive collisions [14]. For investigations of ultrafast molecular dynamics, such as energy and charge transfer across hydrogen bonds in molecular systems, photoion-photoion coincidence measurements at free-electron lasers are developing as a powerful tool [8, 15, 16] and this approach was also used to study hydrogen bonding in the water dimer at a synchrotron [17]. Other spectroscopic techniques utilizing synchrotron facilities [18, 19] or table-top laser-systems [5, 6, 20, 21] further improved the knowledge about hydrogen bonding in water and water-clusters.

Most of these experiments investigating the dynamics of hydrogen-bonded systems would benefit from samples of identical molecules in a well-defined initial state. The widely used supersonic expansion technique provides cold molecular beams down to rotational temperatures of < 1 K [22–24]. However, cluster expansions do not produce single-species beams, but a mixture of various cluster stoichiometries. Hence, only low concentrations of specific species can be achieved. In the case of water molecules, supersonic expansion produces a cold beam of various water clusters [2] with a water dimer concentration of only a few percent [17, 25]. This leads to small experimental event rates and requires long measurement times, e. g., in coincidence detection schemes [16, 17]. These experiments with a mixture of molecules in a molecular beam are only feasible if it can be disentangled which

molecule was actually measured. Therefore, these mixtures severely limit the applicable techniques. A pure beam of water dimers would significantly speed up the measurements, when unwanted backgrounds from carrier gas and larger water-clusters are avoided, or simply enable such experiments.

The electrostatic deflector is an established method to spatially separate the molecules of interest from the carrier gas and to separate different species within a cold molecular beam [26]. This includes the separation of molecular conformers [27–30], individual quantum states of small molecules [31, 32], as well as specific molecular clusters [24, 33, 34]. The deflector was previously utilized in investigations of water, e. g., to determine the rotational temperatures of “warm” molecular beams of water [35], to separate its *para* and *ortho* species [32], and to measure the dipole moment of small water-clusters [36]. Alternatively, separation by the cluster species’ distinct collision cross sections, i. e., by the transverse momentum changes due to scattering with a perpendicular rare-gas beam, was demonstrated [37]; this method is especially amenable to larger cluster sizes [38]. Such spatially separated single-species samples enable, for instance, advanced imaging applications of water-clusters using non-species-specific techniques, as well as the study of size-specific effects and the transition from single-molecule to bulk behavior.

EXPERIMENTAL METHODS

Here, the electrostatic deflector was used to spatially separate water dimers from water monomers as well as larger water-clusters in a molecular beam formed by supersonic expansion. The experimental setup was described previously [26, 39]. Briefly, liquid water was placed in the reservoir of an Even-Lavie valve [23], heated to 55 °C, seeded in 100 bar of helium, and expanded into vacuum with a nominal driving-pulse duration of 19.5 μ s and at a repetition rate of 250 Hz. The produced molecular beam was doubly skimmed, 6.5 cm ($\varnothing = 3$ mm) and 30.2 cm ($\varnothing = 1.5$ mm) downstream from the nozzle, directed through the electrostatic deflector [40] of 154 mm length

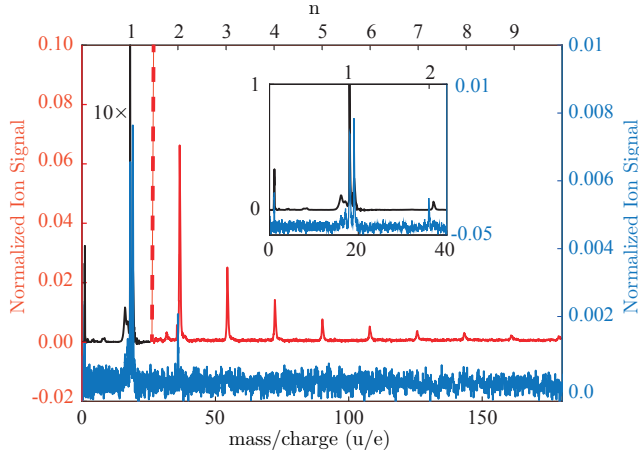


FIG. 1. TOF-MS in the center of the molecular beam as depicted in Fig. 2 with a deflector voltage of 0 kV (black, red) and at a position of +3 mm with a deflector voltage of 8 kV (blue). For mass/charge (m/q) ratios of $0 \dots 30$ u/e, to the left of the dashed red line, the TOF-MS has been scaled by 0.1. The inset shows the region of $m/q = 0 \dots 40$ u/e enlarged; see text for details.

and with a nominal field strength of 50 kV/cm with an applied voltage of 8 kV across the deflector, before passing through a third skimmer ($\varnothing = 1.5$ mm). The deflector was placed 4.4 cm behind the tip of the second skimmer. In the center of a time-of-flight (TOF) mass spectrometer, 134.5 cm downstream from the nozzle, molecules were strong-field ionized by a 35 fs short laser pulse with a central wavelength around 800 nm and a pulse energy of 170 μ J. Focusing to 65 μ m yielded a peak intensity of $\sim 10^{14}$ W/cm². The generated ions were accelerated toward a microchannel-plate detector combined with a phosphor screen and the generated signal was recorded with a digitizer. The valve, skimmers, and deflector were placed on motorized translation stages, which allowed movement of the molecular beam through the ionization laser focus and the recording of vertical molecular-beam-density profiles without moving the laser focus, resulting in fixed imaging conditions [41–43].

While the employed strong-field ionization is a general, non-species specific ionization technique, it can also lead to fragmentation of molecules, such that recorded mass spectra (MS) do not directly reflect the composition of the molecular beam. In combination with the species-specific deflection process, however, this can be disentangled and, thus, even allows for the investigation of strong-field-induced fragmentation processes of a single species.

RESULTS AND DISCUSSION

TOF-MS of the direct and the deflected beams are shown in Fig. 1. The spectrum of the undeflected beam

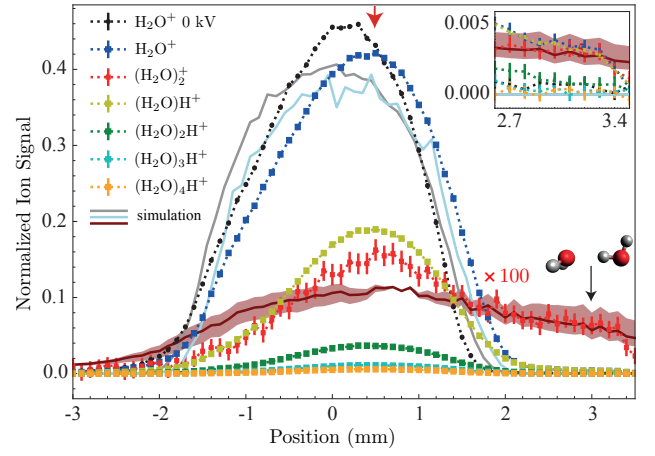


FIG. 2. Normalized measured vertical molecular-beam-density profiles (dashed lines) of water cation (H_2O^+) (blue), water-dimer cation ($(\text{H}_2\text{O})_2^+$) (red), and protonated water-cluster ions ($(\text{H}_2\text{O})_n\text{H}^+$ up to $n = 4$) (yellow, green, cyan, orange) with deflector voltages of 0 kV (black circles) and 8 kV (squares). Simulated vertical molecular-beam-density profiles of the undeflected water monomer (grey) as well as of the deflected water monomer (light blue) and water dimer (dark red) with a deflector voltage of 8 kV are shown as solid lines. The shaded (dark red) area depicts the error estimate of the water dimer simulation due to the temperature uncertainty, $T_{\text{tot}} = 1.5(5)$ K; see text for details. The black arrow indicates the position in the deflected beam where the TOF-MS shown in Fig. 1 was measured. The inset shows the deflection region enlarged with a magnification factor of 5 applied to the $(\text{H}_2\text{O})_2^+$ and $(\text{H}_2\text{O})_n\text{H}^+$ signals.

shows water-cluster ions ($(\text{H}_2\text{O})_n^+$ up to $n = 2$ and protonated water-cluster ions ($(\text{H}_2\text{O})_n\text{H}^+$ up to $n = 10$). Even larger clusters were likely formed in the supersonic expansion, but were not observed in the recorded TOF interval. We point out that all clusters that reach the interaction region are neutral clusters of the type $(\text{H}_2\text{O})_n$, and protonated clusters must result from the interactions with the femtosecond laser, i. e., due to fragmentation during or after the strong-field-ionization process.

Vertical molecular-beam-density profiles for water ions (H_2O^+), water dimer ions ($(\text{H}_2\text{O})_2^+$), and protonated water-cluster ions ($(\text{H}_2\text{O})_n\text{H}^+$ up to $n = 4$), with a potential difference of 8 kV applied across the deflector, are shown in Fig. 2. For comparison, a field-free vertical profile for the water ion with 0 kV across the deflector is also shown. The vertical molecular-beam-density profiles have been normalized to the area of the field-free spatial profile of the water ion. For visibility the water dimer profile has been scaled by a factor of 100 after normalization. While the field-free molecular beam profile is centered around 0 mm, application of a voltage of 8 kV to the deflector shifted the peak of water ions, water dimer ions, and protonated water-cluster ions by +0.5 mm, as indicated by the red arrow in Fig. 2. In addition, water dimer ions

showed a broadening and an increase of signal at around +3 mm, indicated by a black arrow in Fig. 2.

In the inset of Fig. 2 the region around +3 mm is shown enlarged with a magnification factor of 5 applied to $(\text{H}_2\text{O})_2^+$ and $(\text{H}_2\text{O})_n\text{H}^+$ with $n = 1 \dots 4$. The corresponding TOF-MS in the deflected part of the beam at a position of +3 mm is highlighted in Fig. 1 by the blue line. Not just water dimer ions, but also hydronium ions, H_3O^+ , and water ions, H_2O^+ , showed an increased signal in the deflected beam. The shape of the vertical beam profiles for these ions matched the water dimer profile in the region of 2.8–3.5 mm, indicating that they originated from the same parent molecule.

The water dimer ion was the largest non-protonated cluster measured in this setup. To verify that the water dimer ion was originating from the water dimer, the deflection behaviour of water-clusters inside the electrostatic deflector was simulated. Therefore, the Stark energies and effective dipole moments of water monomers and water-clusters were calculated with the freely available CMISTARK software package [44] using rotational constants, dipole moments, and centrifugal distortion constants from the literature [11, 45–48], see Suppl. Inf. Table I; contributions of the polarizability to the Stark effect could safely be ignored [40, 49]. The rotational constants of the water dimer are significantly smaller than for the water monomer, leading to a larger effective dipole moment for the water dimer than for water and a larger acceleration in the electric field in the deflector, see Fig. 3 and Table I of the Suppl. Inf. for further information.

The simulated vertical molecular-beam-density profiles of the water monomer and the water dimer are shown in Fig. 2. The deviations between the measured and simulated undeflected vertical beam profiles are ascribed to imperfect alignment of experimental setup, which was not taken into account in the simulations. Due to the rotational-state dependence of the Stark effect, the deflection of a molecular beam in an electrostatic field depends on the rotational temperature of the molecular ensemble [26] and the best fit for the profiles of the water monomer and the water dimer at a deflector voltage of 8 kV was obtained assuming a Boltzmann population distribution of rotational states corresponding to 1.5(5) K.

Not only deflection of water-clusters measured as a mass of 36 amu, but also of water-clusters detected as protonated-clusters have been measured, for instance, for $(\text{H}_2\text{O})_2^+$, as indicated by the red arrow and symbols in Fig. 2. Trajectory simulations for water-clusters $(\text{H}_2\text{O})_n^+$ with $n = 3 \dots 7$ using a rotational temperature of $T_{\text{rot}} = 1.5(5)$ K were performed to understand the origin of this deflection behavior. For the water hexamer three and for the water heptamer two conformers have been simulated, assuming an equal population of the conformers. These showed that, based on the different effective dipole moments, a different deflection is expected for different water-clusters, see Fig. 5 of the Suppl. Inf.. Since the

detected protonated water-clusters arose from the strong-field fragmentation of larger neutral clusters in the interaction region, the measured vertical protonated-cluster density profiles are a superposition of several neutral water-cluster density profiles. Thus, it is not possible to compare the individual simulated molecular-beam-density profiles of neutral clusters directly with the measured protonated water-cluster density profiles. Instead, at each position of the deflection profile the signal from all water-clusters has been summed up, both for the simulated and the measured molecular-beam-density profiles. The result yields a comparable amount of deflection for simulated and measured molecular-beam-density profiles, see Suppl. Inf. Fig. 6. The shift of 0.5 mm can, therefore, originate from the superimposed molecular-beam-density profiles from different larger clusters due to fragmentation into smaller water-clusters. The same shift is visible for H_2O^+ and $(\text{H}_2\text{O})_2^+$, which indicates that water-clusters are also fragmenting into H_2O^+ and $(\text{H}_2\text{O})_2^+$. Nevertheless, the simulation for water-clusters $n = 1 \dots 7$ shows that the water dimer deflected the most, reaching a position of +3 mm and above, see Suppl. Inf. Fig. 4 and Fig. 5. Of all the other clusters considered, only the water hexamer in its prism and book forms reaches to a position up to 3.2 mm with the falling edge of the profile. In our experiments the water hexamer and higher order clusters have only been measured as fragments, such that the concentration and size distribution of neutral clusters in the molecular beam is unknown. However, the measured fragment distributions strongly suggest that significantly larger clusters are not present, since the ion signals decay exponentially and it is known that clusters primarily fragment through loss of single water molecules [50–52].

The TOF-MS in the deflected part of the beam, shown in Fig. 1, contains peaks corresponding to H^+ , O^+ , OH^+ , H_2O^+ , and H_3O^+ , in addition to the water dimer ion. As mentioned before the short-pulse ionization can lead to fragmentation. For the water dimer, two fragmentation channels were reported for electron-impact ionization with 70 eV electrons [50]: either an H_3O^+ ion and a neutral OH are formed or a H_2O^+ ion and a neutral water monomer H_2O . Using a size-selection method and infrared spectroscopy, H_2O^+ has been reported as a fragment of the water dimer [37]. Comparison of the vertical molecular-beam-density profiles of the deflected molecules allowed further investigation of the fragmentation channels of the water dimer. The measured vertical molecular-beam-density profiles of these molecules showed a similar deflection behavior in the region of 2.8 to 3.5 mm as the water dimer, see Fig. 2 and Suppl. Inf. Fig. 1. The observed constant ratio of those fragments over this spatial region indicates that all these fragments originated from the water dimer.

Comparing the intensity of the fragments of the water dimer, H_2O^+ and H_3O^+ and $(\text{H}_2\text{O})_2^+$, in the deflected beam, the fragmentation ratios of the intact water dimer

were estimated. These showed that 46(7) % of the water dimer fragmented into one ionized water molecule, while 46(4) % of the water dimer underwent most likely proton transfer and formed a hydronium ion. Only 8(2) % of the water dimer present in the molecular beam stayed intact after ionization.

The actual number of water dimer molecules per shot in the deflected molecular beam was estimated to ~ 0.8 within the laser focus using the known fragmentation ratios of H_2O^+ and H_3O^+ , while the fragmentation channels of H^+ , O^+ , OH^+ have not been included. Taking the known fragmentation channels into account, the fraction of the water dimer within the molecular beam was evaluated. Comparing the ratios between the water dimer and all other species visible in the TOF, a water dimer fraction of 3.9(6) % in the center of the undeflected beam and of 93(15) % in the deflected beam, at a position of +3 mm, was achieved. Thus, using the electrostatic deflector the fraction of the water dimer within the interaction region could be increased by nearly a factor of 24.

CONCLUSIONS

In summary, a high-purity beam of water dimers was created using the electrostatic deflector, which spatially separated water dimers from other species present in the molecular beam. The resulting water dimer sample had a purity of 93(15) %. The fragmentation products and ratios of the water dimer following strong-field ionization using a 35 fs laser pulse with a wavelength centered around 800 nm and peak intensity of $\sim 10^{14}$ W/cm² were studied, with 46(4) % of the water dimer found to form a hydronium ion and 46(7) % fragmenting into one water cation and one neutral water monomer, while 8(2) % of the water dimer stayed intact. The deflection profiles could be simulated using a rigid-rotor model and an initial rotational temperature of 1.5(5) K.

The produced clean samples of water dimers are well suited for non-species-specific experiments, e.g., reactive-collisions, diffractive imaging, or ultrafast spectroscopies [14, 41, 53]. Even for experiments that can distinguish different species, for example photoion-photoion coincidence measurements [8, 54], the produced clean beams will enable significantly faster measurements of this important hydrogen-bonded model system, e.g., because unwanted backgrounds are avoided. Furthermore, the electrostatic separation technique can be used to separate different conformers [26], which could be highly interesting in the purification and studies of larger water-clusters that exhibit multiple conformers [55].

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SUPPORTING INFORMATION DESCRIPTION

Supporting Information Available: Description of the fragmentation correction method and the trajectory simulations

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Supplemental Material: Pure molecular beam of water dimer

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FRAGMENTATION CORRECTION OF MEASUREMENTS

The strong-field-ionization technique employed in this work can lead to fragmentation, such that clusters from the molecular beam contributed to smaller masses in the mass spectrum (MS). For example, the water monomer and the water dimer signals at $m/q = 18$ u/e and 36 u/e, respectively, contained contributions due to fragmentation of larger water-clusters in the molecular beam. Therefore, measured intensities needed to be corrected for these fragmentation channels. In addition, background water inside the chamber was measured at 18 u/e and needed to be corrected for.

For the latter, background measurement were permanently performed during the experiments using the higher repetition rate of the laser compared to the valve. Laser pulses were arriving in the interaction region at the same time as the molecular beam and between two molecular beam pulses, such that for each data point a background measurement was performed. The background signal was subtracted from the measurements.

The fragmentation ratios of the water dimer into smaller masses could be estimated and used for the calculation of the fraction of the water dimer in the deflected and undeflected molecular beam [1]. In Fig. 1 the deflection profiles measured at masses corresponding to H^+ , O^+ and OH^+ are shown. In the region of 2.8 to 3.5 mm the deflection curves look identical to those for the water dimer, indicating that at these positions those are fragments from the water dimer. The ratios of the water dimer to H^+ , O^+ and OH^+ at a position of 3 mm are 0.3, 0.8, and 0.7, respectively. For the calculation of the fraction of the water dimer in the molecular beam for the undeflected beam, these ratios were used to estimate the amount of the water dimer inside of the beam.

For larger clusters, only fragments were measured, such that the measured signal was not solely due to a specific cluster stoichiometry and the overall shape of the molecular beam profile arose from several larger water-clusters. All protonated-water-cluster ions recorded showed the same deflection behavior, see Fig. 2. An estimate of the exponential decay of the measured protonated water-clusters distribution showed that protonated water-clusters $n = 1 - 10$ contained 99.6 % of the overall intensity.

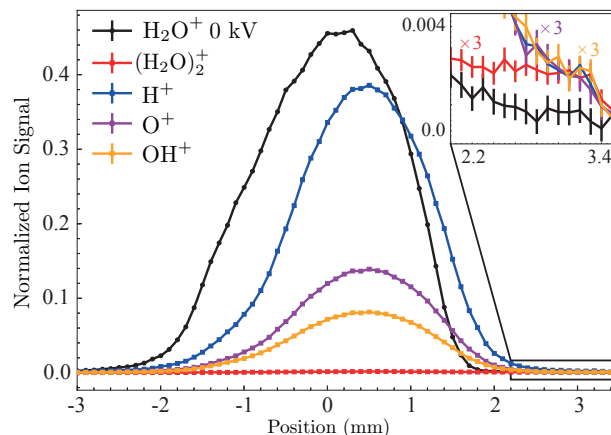


FIG. 1. Column density profiles, measured for the water-monomer cation with deflector voltages of 0 kV (black) and for H^+ (blue), O^+ (purple), OH^+ (orange) and the water-dimer cation with a deflector voltage of 8 kV (red). The inset shows the region around $y = 3$ mm enlarged, with O^+ , OH^+ and the water dimer ion scaled by a factor 3.

TRAJECTORY SIMULATIONS

The Stark energies and effective dipole moments μ_{eff} of water-clusters $n = 1 \dots 7$ were calculated using the freely available CMISTARK software package [2], which were then used to perform trajectory simulations [3] and to verify the measured deflection profiles of water-clusters. The rotational constants, dipole moments and centrifugal distortion constants from the literature are summarized in Table I. Three conformers for the water hexamer in prism-, book- and cage-like form [13] and two conformers of the water heptamer following the naming scheme of [15] were included.

For these simulations the water-clusters were assumed to be rigid rotors. Since the water dimer is known to be a floppy molecule with large amplitude motions [7, 16], the corresponding energy spectra and the description of the interaction of the states would significantly complicate further analysis. Using a rigid rotor assumption enables an easier and faster description and it has been shown previously that this model can be used to describe the dynamics of indole(H_2O) in strong-electric- and laser-field alignment and orientation experiments [17, 18] and to fit pure rotational transitions of the water dimer to

molecule	dipole moment μ (D)			rotational constants (MHz)			Centrifugal Distortion constants (kHz)							
	μ_a	μ_b	μ_c		A	B	C	Δ_J	Δ_{JK}	Δ_K	d_J	d_K		
H ₂ O	0	-1.86	0	[4]	835840.29	435351.72	278138.70	[5]	3.759×10^{-4}	-1.729×10^{-5}	9.733×10^{-5}	1.521×10^{-4}	4.105×10^{-4}	[5]
(H ₂ O) ₂	2.63	0	0	[6]	190327.0	6162.76	6133.74	[7]	0.044	4010	0	0	0	[8]
(H ₂ O) ₃	0	0	0	[9]	6646.91	6646.91	0	[10]	—	—	—	—	—	
(H ₂ O) ₄	0	0	0	[9]	3149.00	3149.00	1622.00	[11]	—	—	—	—	—	
(H ₂ O) ₅	0.93	0	0	[9]	1859.00	1818.00	940.00	[12]	—	—	—	—	—	
(H ₂ O) ₆ book	0.17	2.46	0.16	[13]	1879.47	1063.98	775.06	[13]	—	—	—	—	—	
(H ₂ O) ₆ cage	1.63	0.32	1.13	[13]	2163.61	1131.2	1068.80	[14]	—	—	—	—	—	
(H ₂ O) ₆ prism	2.41	0.88	0.42	[13]	1658.22	1362.00	1313.12	[13]	—	—	—	—	—	
(H ₂ O) ₇ 1	1.0	1.0	0.0	[15]	1304.44	937.88	919.52	[15]	0.457	-0.342	0.842	0.0377	0.63	[15]
(H ₂ O) ₇ 2	1.0	0.0	1.0	[15]	1345.16	976.88	854.47	[15]	0.044	0.000	0.000	0.0000497	0	[15]

TABLE I. Dipole moments, rotational constants and centrifugal distortion constants of water-clusters used in the Stark-effect calculations

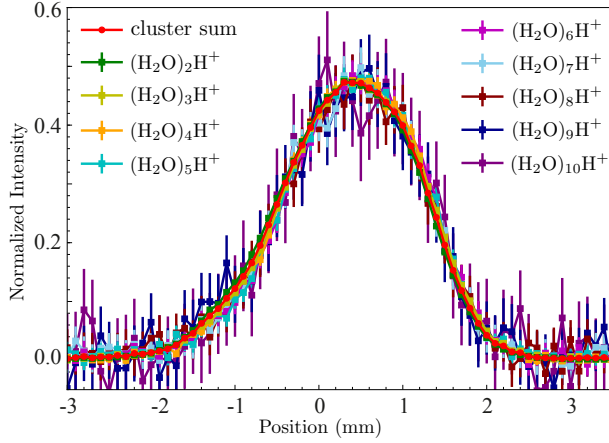


FIG. 2. Comparison of the averaged measured protonated-water-cluster signal (red) and the individual measured protonated water-clusters deflection profiles for $n = 2 \dots 7$. The profiles are normalized to the area under the curve.

experimental measurements [8].

For the rotational states $J = 0 \dots 2$ of the water monomer and the water dimer the Stark energies and the corresponding μ_{eff} as a function of the electric field strength are shown in Fig. 3. For the water dimer all relevant states are strong-field seeking and, hence, accelerated toward regions of stronger fields. For a nominal field strength of 50 kV/cm the μ_{eff} of the water dimer are significantly larger than for the water monomer, except from the $|J, K_a, K_c, M\rangle = |2, 0, 2, 0\rangle, |2, 1, 1, 1\rangle$ states, leading to a larger acceleration in the electric field. All the shown states have a small asymmetry splitting, see Table I, resulting in a fast rise of μ_{eff} at small electric field strength. The discontinuous change of μ_{eff} at an electric field around 30 kV/cm is ascribed to an avoided crossing of the $|2, 2, 0, 2\rangle$ and $|3, 2, 2, 2\rangle$ states.

The trajectories of the molecules inside the electrostatic deflector were simulated using the calculated μ_{eff} [3]. For quantum states $J = 0 \dots 10$, 10^7 trajectories were calculated for each set of J states and used to simulate the spatial profiles using a weighting factor based on the thermal distributions of the state for a given temper-

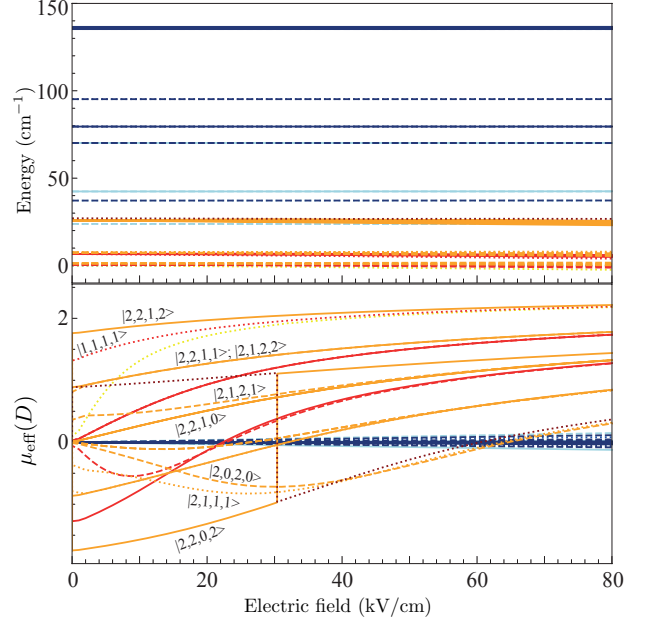


FIG. 3. Calculated Stark energy and effective dipole moments for the $J = 0 \dots 2$ states of the water monomer (blue) and the water dimer (red, orange, yellow). $J = 0$ are shown in blue (water) and yellow (water dimer), $J = 1$ in light blue (water), red (water dimer), $J = 2$ in darkblue (water) and orange (water dimer) and the $|3, 2, 2, 2\rangle$ state in darkred for the water dimer. States where $K_a < K_c$ are indicated by dashed lines, $K_a > K_c$ by solid lines and $K_a = K_c$ by dotted lines.

ature. Those temperature-weighted simulated vertical molecular-beam profiles were scaled to the area under the curve of the corresponding experimental profile to compare the deflection profiles. The simulations include the nuclear-spin-statistical weights for the water monomer and the water dimer. For *para*- and *ortho*-water a room-temperature distribution of 1 : 3 was used. The water dimer in its equilibrium geometry is isomorphic with the permutation-inversion point group D_{4h} including tunneling splittings [19]. Neglecting tunneling splittings and acceptor switching, the rigid water dimer belongs to the symmetry group $C_S(M)$, yielding nuclear-spin-statistical

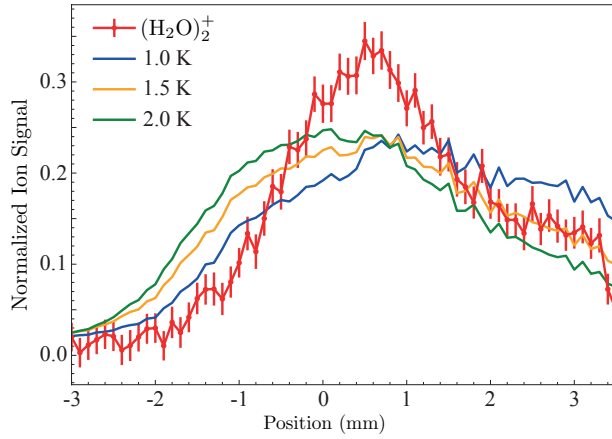


FIG. 4. Simulated deflection profiles for the water dimer at temperatures of 1.0 K, 1.5 K and 2 K compared to the corrected pure water dimer profile at 8 kV (red, dots).

weights of *para:ortho* of 16 : 16 [20].

The simulated profiles for the water dimer at different rotational temperatures T_{rot} including rotational states $J = 0 \dots 10$ are shown in Fig. 4. An initial-beam temperature of $T_{\text{rot}} = 1.5(5)$ K reproduced the experiment the best. At this temperature the water monomer in the *para* nuclear spin state has 100 % of its population in its absolute rotational ground states $|J = 0, K_a = 0, K_c = 0, M = 0\rangle$, while *ortho*-water populates the $|J = 1, K_a = 0, K_c = 1, M = 0, 1\rangle$ state to equal amounts. 99.9 % of the *para*-water dimer and 99.9 % of the *ortho*-water dimer population is within $J = 0 \dots 10$.

Trajectory simulations were performed for water-clusters up to $n = 7$. Based on the estimated water-cluster distribution, *vide supra*, this covers 97.8 % of the water-clusters in the molecular beam, while ~ 2.2 % of the molecules in the beam are from water-clusters $n \geq 8$. The simulations for water-clusters including $J = 0 \dots 2$ and using the same rotational temperature $T_{\text{rot}} = 1.5(5)$ K of the water dimer are shown in Fig. 5. We note that at this temperature rotational states up to $J = 10$ might be populated in the molecular beam and the rotational temperature can differ from the one of the water dimer. Thus the simulations give just an estimate of the amount of deflection. Based on the simulations the water dimer is deflecting the most of all water-clusters, followed by the water hexamer in prism- and book-like form, which reaches to a position of +3.2 mm.

Since for larger clusters only fragments have been measured and, therefore, the shape of the recorded beam profiles is the result of a superposition of several neutral cluster distributions in the molecular beam, it is not possible to compare the single deflection profiles directly with simulations. Therefore, at each position of the deflection profile the signal of the measured protonated water-clusters for $n = 2 \dots 10$ have been summed up. The

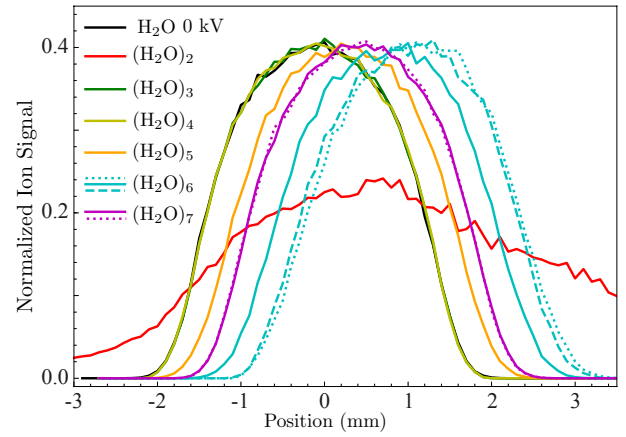


FIG. 5. Simulated deflection profiles for water-clusters for $n = 2 \dots 7$ are shown. Three different conformers of the water hexamer and two of the water heptamer were included, see text for details.

H_3O^+ , $n = 1$, contained also signal from the water dimer and has not been included. For the computationally derived profiles $n = 3 \dots 7$ were summed up for each position. As for the hexamer and heptamer several conformers have been simulated, each profile of the hexamer has been divided by 3 and for the heptamer by 2. This is shown in Fig. 6. These simulations assume a rather low temperature of 1.5 K and did not include the needed nuclear spin statistical weighting for larger-clusters. In addition, the decaying water-cluster distribution in the molecular beam was not taken into account, resulting in a slightly different shape of the vertical molecular-beam-density profiles than

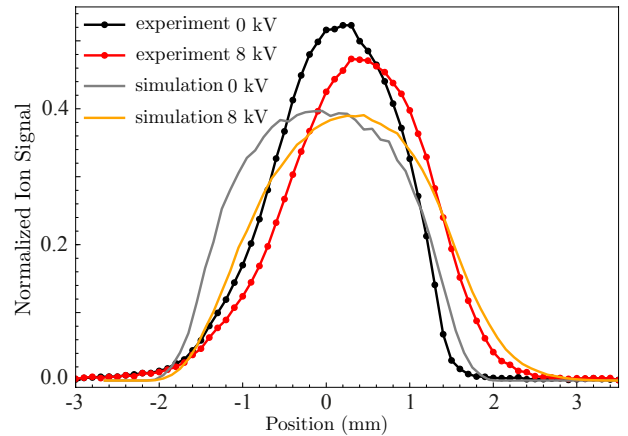


FIG. 6. Summed up simulated deflection profiles for water-clusters for $n = 3 \dots 7$ (grey, orange) and summed up measured deflection profiles for protonated water-clusters for $n = 2 \dots 10$ (black and red dots) for a deflector voltage of 0 kV (grey, black) and 8 kV (orange, red). The profiles are normalized to the area under the curve.

the measured ones. However, comparing the simulated and the measured deflection profiles, the deflection is on the same order of magnitude and the right-hand side tail of the simulated deflection profile is reaching up to a position of +3.2 mm.

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