PAPER

Photochemistry and UV/vis spectroscopy of hydrated vanadium cations, $V^+(H_2O)_n$, $n = 1–41$, a model system for photochemical hydrogen evolution†

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Photochemical hydrogen evolution provides fascinating perspectives for light harvesting. Hydrated metal ions in the gas phase are ideal model systems to study elementary steps of this reaction on a molecular level. Here we investigate mass-selected hydrated monovalent vanadium ions, with a hydration shell ranging from 1 to 41 water molecules, by photodissociation spectroscopy. The most intense absorption bands correspond to 3d–4p transitions, which shift to the red from $n = 1$ to $n = 4$, corresponding to the evolution of a square-planar complex. Additional water molecules no longer interact directly with the metal center, and no strong systematic shift is observed in larger clusters. Evolution of atomic and molecular hydrogen competes with loss of water molecules for all $V^+(H_2O)_n$, $n \leq 12$. For $n \geq 15$, no absorptions are observed, which indicates that the cluster ensemble is fully converted to HVOH+(H2O)−1. For the smallest clusters, the electronic transitions are modeled using multireference methods with spin–orbit coupling. A large number of quintet and triplet states is accessible, which explains the broad features observed in the experiment. Water loss most likely occurs after a series of intersystem crossings and internal conversions to the electronic ground state or a low-lying quintet state, while hydrogen evolution is favored in low-lying triplet states.

Introduction

The hydrogen evolution reaction will play an important role in future energy systems that rely on renewable energies.¹ Transforming electricity from solar or wind power stations to hydrogen in large-scale electrolyzers paves the way to a carbon-neutral transportation sector, where e.g. hydrogen powered trains equipped with fuel cells² are already in service. On a molecular scale, hydrogen evolution at metal centers exhibits a fascinating variability.³ Hydrogen atom formation is observed in Mg+(H2O) in the gas phase within a relatively narrow size range.⁴-⁶ A series of quantum chemical studies indicated that the H atom is formed via the recombination of a proton with a hydrated electron, which forms spontaneously as soon as at least six water molecules are available.⁷-¹¹ We recently confirmed the presence of a hydrated electron in Mg+(H2O)ₙ, $n > 20$, by photodissociation spectroscopy,¹² where the typical broad absorption of the hydrated electron¹³,¹⁴ was observed. The corresponding aluminum species, Al+(H2O)ₙ, eliminate H₂ in a thermally activated reaction,¹⁵,¹⁶ consistent with the preferred oxidation state +III of the metal center. Here, hydrogen evolution takes place in two steps, insertion of Al⁺ into an O–H bond via a concerted proton transfer results in the HAOH+(H2O)−₁ structure, from which H₂ evolves via a proton-hydride recombination, again mediated by concerted proton transfer through water wires.¹⁷-¹⁹

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‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/d1cp02382a
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Received 28th May 2021, Accepted 6th August 2021
DOI: 10.1039/d1cp02382a
rsc.li/pccp
While the computational studies confirmed the key mechanistic features in the magnesium and aluminum systems, important aspects are still to be resolved. In the aluminum system, H/D exchange reactions with D₂O revealed that concerted proton transfer does not take place in clusters with more than 40 water molecules. The transition metal vanadium exhibits a larger variability of oxidation states, and V(H₂O)ₙ clusters eliminate both atomic and molecular hydrogen, again with a very specific size dependence. Isotopic scrambling in H₂O/D₂O exchange is consistent with formation of the inserted structure HVOH⁺(H₂O)ₙ₋₁ and the H₂ elimination product V(OH)₂⁺(H₂O)ₙ₋₂ in the size regime \( n \leq 24 \). This conclusion is challenged in recent work by Ng and co-workers, who use state-selected V⁺ ions. They report efficient VO⁺ formation from the V⁺(a¹D) ground state at center of mass energies below 3 eV, which is energetically only possible if molecular H₂ is formed. Ng and co-workers agree with the Armentrout group that the triplet state is significantly more reactive. Overall, they conclude that the reaction is governed by a weak quintet-triplet spin crossing mechanism. The importance of the triplet state in the reaction of V⁺ with H₂O was confirmed in a quantum chemical study by Ugalde and co-workers. Water molecules in collisions with neutral and cationic vanadium clusters Vₙ⁺ were found by Luo and co-workers to undergo H₂ elimination and formation of VₙO⁺. In the present study, we re-investigate the photochemistry of V(H₂O)ₙ⁺, \( n = 1-4 \), using a tunable optical-parametric oscillator (OPO) system to extend both wavelength range and resolution and to increase sensitivity due to its high spectral radiation density. We then continue to clusters with up to 41 water molecules to learn more about the electronic and geometric structure in the cluster-size regime where thermally activated hydrogen evolution occurs. Quantum chemical calculations including electronically excited states are used to assign the spectral transitions and to rationalize the observed photochemical reactivity.

### Experimental methods

The experiments are performed on a modified Bruker Spectrospin CMS47X 4.7 T Fourier-Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS). The clusters are created by vaporization of a vanadium target with a frequency doubled Nd:YAG laser. The ions are picked up by a supersonic beam of He seeded with water vapor. In the ICR cell, the clusters are mass selected and irradiated with light in the range of 296–2600 nm provided by an EKSPLA NT342B Optical Parametric Oscillator (OPO), running at 20 Hz repetition rate. The fragmentation yield is controlled via the number of laser shots, usually in the range of 5 to 20 shots, which corresponds to irradiation times of 0.25 to 1 s.

After irradiation, a mass spectrum of the precursor ion and the photofragments is measured and the absorption cross section can be calculated. Ions with \( m/z \) corresponding to [VOH(H₂O)ₙ⁺], [VO(H₂O)ₙ⁺] and V⁺(H₂O) are observed after irradiation (see Fig. S6 for a sample spectrum, ESI†), with branching ratios that strongly depend on the cluster size of the precursor ion and the irradiation wavelength. The laser power was measured after recording each mass spectrum to compensate fluctuations. Due to the different optical stages used in the OPO system, the beam may shift slightly or change its profile when switching to a different OPO stage, e.g. from signal to sum frequency generation (SFG). This leads to a different overlap of the beam with the ion cloud. To compensate for these effects, the cross section in the SFG stage of the OPO, \( \lambda < 410 \) nm, is multiplied with a scaling factor to ensure continuity. As a reference, the cross section in the signal stage was used, since the beam quality is the best in this stage and the power...
measurement has the smallest error.\textsuperscript{52,53} The signal UV correction factor for \( n = 1 \) and 2 uses the average scaling factor of the clusters with \( n = 3–41 \) since there are no absorptions at the signal/SFG switch point, see Table S2 (ESI\textsuperscript{†}). The walls of the ICR cell are cooled with liquid nitrogen to a temperature of about 83 K to reduce black body infrared radiation dissociation (BIRD).\textsuperscript{54–60} Due to the supersonic expansion in helium buffer gas, the ions leave the cluster source region with internal energy far below room temperature, as directly evidenced by the large water clusters forming in the source. In the practical absence of collisions in the cryo-pumping environment of the cooled ICR cell, exchange of infrared radiation between the ion and the cell walls subsequently equilibrates the ions to about 83 K.

Despite the significantly increased stability of even the largest clusters studied, some fragmentation due to BIRD is still observed, especially for large clusters. Therefore, photodissociation spectra of cluster sizes \( n > 15 \) are BIRD corrected by subtracting fragment intensities of a reference mass spectrum from the fragment intensities of mass spectra used in calculating the photodissociation cross section. For the reference mass spectrum, the ions are stored without irradiation for the same duration as in the corresponding spectroscopy experiment.

**Results and discussion**

**Photodissociation of V\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{1–4}**

**Experimental spectra.** The measured photodissociation cross sections for \( n = 1–4 \) are shown in Fig. 1. As shown in previous studies,\textsuperscript{33,35,41} all water molecules in these clusters are intact and coordinate in a near-planar geometry, without any water–water hydrogen bonding. Our calculations predict a planar V\textsuperscript{+}(H\textsubscript{2}O), a quasi-linear V\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{2}, a Y-shaped V\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{3} and square-planar V\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{4} in \( C\textsubscript{2v}, D\textsubscript{3h}, C\textsubscript{4v} \) and \( C\textsubscript{4h} \) symmetry, respectively, overall in agreement with previous infrared experiments.\textsuperscript{35,41} For \( n = 3 \), the T-shaped isomer reported by Ohashi and co-workers\textsuperscript{35} is within error limits isoenergetic with the Y-shaped structure from Fig. 1, and exhibits a small imaginary frequency in our calculations. This indicates that the position of the oxygen atoms is not very well defined for this cluster size and that the water molecules undergo large-amplitude motions even at low temperatures in the coordination plane of the metal center for \( n = 3 \).

The intense excitations of the clusters continuously red-shift and broaden with increasing cluster size. Three qualitatively different fragmentation channels are observed, namely the loss of \( x\textsubscript{2}H\textsubscript{2}O \), \( H\textsubscript{2} + x\textsubscript{2}H\textsubscript{2}O \) and \( H + x\textsubscript{2}H\textsubscript{2}O \) in agreement with previous experiments utilizing a high-pressure mercury arc lamp.\textsuperscript{33} The number of water molecules lost upon absorption of a single photon depends on the photon energy, the internal energy of the cluster before the absorption event and the cluster size.

In the spectrum of V\textsuperscript{+}(H\textsubscript{2}O), two features peaking at 2.05 and 2.45 eV can be seen in the lower photon energy range of 1.9–2.5 eV. In the range of 1.9–2.2 eV, the loss of water dominates the fragmentation yield. In a previous molecular beam study by Lessen \textit{et al.},\textsuperscript{40} the water loss channel was used to measure a photodissociation spectrum, which implies that it was also the dominant channel there. The onset of this transition was found to lie at 1.97 eV (15 880 cm\textsuperscript{-1}) with a progression of 0.04 eV (340 cm\textsuperscript{-1}) indicating a vibrationally resolved spectrum.\textsuperscript{40} Since we are covering a much wider energy range in the present study, we chose a step width of 10 nm in this region, which does not allow us to identify the vibrational levels. The staggered data points may thus, at least in part, reflect the original vibrational structure. However, we have reason to assume that the spectrum is significantly broadened in our experiment. Even at the relatively low temperature of 83 K, several rotational levels are populated, which, in view of the large rotational constant \( A = 13.7 \) cm\textsuperscript{-1} of the near-prolate rotor, leads to a rotational broadening on the order of 30 cm\textsuperscript{-1}.

In addition, all electronic states, including the ground state, are subject to spin–orbit splitting. In the V\textsuperscript{+} [Ar]3d\textsuperscript{4} ground state...
configuration, the spin–orbit coupling leads to five spin–orbit states from 0 to 339 cm$^{-1}$. In $\text{V}^+(\text{H}_2\text{O})_n$, $n = 1–4$. The noise level is shown with the grey shaded area. Weak transitions are scaled as indicated for better readability. Solid lines represent a three-point running average. The corresponding calculated oscillator strength $f$ is shown for $n = 1–3$ as orange vertical lines, including spin–orbit coupling for $n = 1, 2$, on the MRCI(4,9)/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ level of theory. For $n = 1$, the MRCI(10,12)/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ calculation of quintet states including the Davidson correction is added as violet vertical lines.

In contrast, the absorptions above 3.7 eV of $\text{V}^+(\text{H}_2\text{O})_n$ are redshifted, starting now at 3.4 eV. The cross-section maxima are located at 2.50, 2.70, 3.50 and 3.85 eV. Across all bands, the dominant decomposition channel is the loss of one H$_2$O molecule while loss of molecular or atomic hydrogen exhibit a lower intensity. The latter two may be accompanied by loss of H$_2$O. While water loss is exclusively observed in the low energy feature, the other two decomposition pathways become more competitive towards higher energies, with H$_2$ loss always favored over H loss.

The intense absorption features broaden and further shift to the red for $\text{V}^+(\text{H}_2\text{O})_3$, peaking at 3.05 eV. Two broad bands are found on either side of the main absorption, and a weak broad band emerges around 1.15 eV. Water loss dominates the photodissociation spectrum, with H$_2$ loss as the second most intense fragmentation channel for the most part of the spectrum. H atom loss again becomes more competitive with increasing photon energy, surpassing H$_2$ loss above 3.4 eV, albeit at an overall low level.

The main absorption shifts further to the red for $\text{V}^+(\text{H}_2\text{O})_4$, with a maximum at 2.70 eV, about 1 eV lower than for $n = 1$. While water loss is again the dominant dissociation channel, H atom

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**Fig. 1** Experimental total photodissociation cross section $\sigma$ along with the partial cross sections of the different dissociation channels for $\text{V}^+(\text{H}_2\text{O})_n$, $n = 1–4$. The noise level is shown with the grey shaded area. Weak transitions are scaled as indicated for better readability. Solid lines represent a three-point running average. The corresponding calculated oscillator strength $f$ is shown for $n = 1–3$ as orange vertical lines, including spin–orbit coupling for $n = 1, 2$, on the MRCI(4,9)/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ level of theory. For $n = 1$, the MRCI(10,12)/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ calculation of quintet states including the Davidson correction is added as violet vertical lines.
elimination is far more intense than H₂ formation. H loss even becomes the dominant fragmentation channel at about 3.4 eV.

**Calculated spectra.** Calculations on the MRCI(4,9)/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ level of theory predict a large number of electronically excited states, shown as vertical lines in Fig. 1. In the ground state configuration of V⁺(H₂O), three 3d orbitals and one 3d–4s hybrid orbital are singly occupied. The two most intense transitions at 3.45 and 3.80 eV correspond to 3d–4p excitations on the vanadium center. These are shifted by about 0.3 eV towards lower energies compared to the experiment, mainly due to the limited active space used in the MRCI calculations. If the active space is enlarged to (10,12) in addition to applying the Davidson correction to estimate the effect of higher-order excitations, the UV transitions shift towards higher excitation energies by about 0.25 eV, almost reaching the experimental value. This confirms that the applied active space in combination with the truncated configuration interaction limits the accuracy of the presented calculations. Between 1.9 and 2.6 eV, the calculations predict many spin-forbidden transitions into triplet and singlet states, which can mix with further quintet states in this range through spin–orbit coupling. Two of these excitations at 2.00 and 2.50 eV exhibit a minor oscillator strength. While the energetic position agrees with the experiment, the intensity mismatches by a factor of about 30 compared to the intense transitions. However, these almost forbidden transitions will gain in intensity upon considering thermal excitation of the system, which breaks the C₂v symmetry, in particular the low-frequency out-of-plane vibration at 217 cm⁻¹. Additionally, the calculations predict a relatively intense band at about 1.40 eV, corresponding to the vanadium 3d–3d excitations. However, this absorption is missing from the experimental spectrum entirely since the photon energy is not sufficient for dissociation. This is in line with the dissociation energy of 1.52(5) eV measured by the Armentrout group, see Table S3 (ESI†).

In V⁺(H₂O)₂, the lowest lying transitions (3d–3d) around 1 eV lose their oscillator strength and are again not observed. The mixed singlet/triplet/quintet transitions responsible for the first two bands in V⁺(H₂O) between 1.9 and 2.5 eV are blue-shifted compared to V⁺(H₂O). The electronic ground state is better stabilized by the second water molecule than the excited states, in agreement with the experiment. In the equilibrium geometry, the transitions lose their oscillator strength completely. This is likely caused by the high D₂h symmetry of the system. The excitations again gain some oscillator strength through thermal population of low-lying vibrational modes, e.g., the two O–V–O bending modes, which break the symmetry. Experimentally, the integrated oscillator strength at 1.9–3.0 eV is actually higher than for V⁺(H₂O). The two most intense bands (3d–4p) in the calculations at ~3.0 and 3.5 eV are red-shifted by about 0.30–0.40 eV compared to V⁺(H₂O). These trends are in good agreement with the experimental observation.

For V⁺(H₂O)₃, an intense 3d–4p band is further redshifted, while the higher-energy bands decrease in intensity. A 3d–3d transition gains a small amount of oscillator strength. Thermal population of low-lying vibrational modes is probably sufficient to mobilize the water molecules in the coordination plane of V⁺ already at 83 K, which would explain the substantial broadening of the bands. Since the highest-energy band decreases in intensity, several other 3d–4p transitions around 3.2 eV exhibit a similar oscillator strength for V⁺(H₂O)₄, corresponding to the very broad feature at about 3.6 eV in the experiment. The position of the experimentally observed 3d–3d transition along with the redshift of the intense UV transition is reproduced well by the calculations. MRCI calculations become too demanding for clusters with n ≥ 4. However, the red shifting of the most intense transition can be expected to continue until the vanadium cation reaches its preferred square-planar coordination in V⁺(H₂O)₄. The low-energy band is missing from the experiment. Here the symmetric solvation of the vanadium cation probably leads to very low oscillator strengths for this excitation, similar to V⁺(H₂O)₂.

**Photochemistry.** To investigate the photochemical decomposition pathways, we scanned the V⁻(H₂O) and the [V(OH)]⁻–H distance in the quintet and triplet manifold, see Fig. 2 and Fig. S5 (ESI†), respectively. As expected, degenerate electronic states of V⁺ are split in V⁺(H₂O). While many conical intersections and intersystem crossings are conceivable along the V–O coordinate, Fig. 2, the excited states run almost parallel to each other along the O–H coordinate in the energy range around the Franck–Condon (FC) point, Fig. S5 (ESI†).

In the FC region, groups of close-lying quintet states are well separated from each other, especially for the states around 3.5–4.1 eV vertical excitation energy. Since thermal energy in this small system is not sufficient to reach a conical intersection, the molecule would become trapped in this group of quintet states if spin were strictly conserved. However, a large number of dense-lying triplet states are available in this energy region (Fig. 2). This allows the system to undergo a sequence of intersystem crossings (ISC) and internal conversions (IC).
through conical intersections to reach the quintet ground state, and any state in between.

We also calculated all relevant transition states (TS) for the three decomposition channels on the B3LYP/aug-cc-pVDZ level of theory in the quintet ground state and the lowest-lying triplet state, see Fig. 3a, building on the calculations by Ugalde and co-workers for the H₂ elimination pathways of V⁺(H₂O).⁴⁷ Water loss requires 1.60 eV and 2.53 eV in quintet and triplet state, respectively, being the energetically preferred decomposition pathway in the quintet state. However, the insertion of the vanadium ion into the water O–H bond is energetically favored in the triplet state, at 2.03 eV for TS1 compared to 2.13 eV in the quintet state. The second transition state towards H₂ loss on the triplet potential energy surface (PES), TS3, lies 0.40 eV below TS1, making H₂ loss the energetically favored dissociation pathway in the triplet state, with the products lying only 0.96 eV above the global minimum of quintet spin multiplicity. All values and geometries are very similar to the results reported by Ugalde and co-workers.⁴⁷ Here we additionally considered H atom. For this channel, the energetically most facile path also proceeds via V⁺ insertion into the O–H bond, followed by loss of the hydrogen atom bound to the metal at 2.34 eV as the direct dissociation needs to overcome a transition state for the charge transfer (TS2) at 2.50 eV.

Based on these findings we can explain the experimentally observed decomposition channels via the simplified scheme in Fig. 4. Due to the dense manifold of triplet and quintet states, intersystem crossing and internal conversion to the quintet ground state and lowest lying triplet state is possible, as well to most, if not all, states in between. The product branching ratio depends on the available energy and photodynamics including several tens of electronic states, which makes a quantitative

Fig. 3  Simplified potential energy surface of the lowest lying triplet state and quintet electronic state to follow the decomposition channels of (a) V⁺(H₂O) (b) V⁺(H₂O)₂, (c) V⁺(H₂O)₃ and (d) V⁺(H₂O)₄ towards H₂O loss, H₂ formation and H loss on the B3LYP/aug-cc-pVDZ level of theory. Only key steps of the PES for the decomposition are shown while missing minima or transition states are indicated via "...". H₂O and H₂ loss PES of V⁺(H₂O) similar to (a) have been reported previously.⁴⁷
and directly competes with the formation of H\(_2\), which requires the production of a hydrogen radical. This channel is entropically favored in the second band, the photon energy is sufficient for the dissociation of H\(_2\)O, 46 and attributed this to weak spin–orbit coupling in V\(^+\) (H\(_2\)O), 65,66 verified that the ions in the present study are predominantly by water loss on the quintet PES. The situation is inherently weak spin–orbit coupling in V\(^+\), but rather by the missing crossing of the quintet ground state and the lowest-lying triplet state PES.

Depending on the spin–orbit coupling between the five lowest triplet states and the three lower-lying quintet states, the system might evolve for an extended period of time on the triplet surface. Two subsequent ISCs in the flat region of the potentials, where the five lowest triplet states encounter the higher-lying quintet states, afford relaxation to the lowest-lying triplet states. If the system has enough kinetic energy, isomerization or dissociation might take place on a low-lying triplet PES, most likely the lowest-lying triplet state, which favors H and H\(_2\) loss over H\(_2\)O evaporation, see Fig. 3a. Only in the first experimental band, where the energy is insufficient or barely sufficient for water splitting, the ion has enough time to return into the quintet state manifold and decompose predominantly by water loss. In CID experiments performed by Armentrout and co-workers, no VO\(^-(\text{H}_2\text{O})\) or VOH\(^-(\text{H}_2\text{O})\) formation has been observed with up to 5 eV center-of-mass collision energy for \(n = 1-4\).\(^{34}\) CID experiments on our instrument\(^{45,66}\) verified that the ions in the present study are not structural isomers, \(e.g.,\) with a vanadium ion inserted into an O–H bond. The results are consistent with the guided ion

**Fig. 4** Schematic photochemical relaxation processes in the V\(^+(\text{H}_2\text{O})\) system involving internal conversion (IC) and intersystem crossing (ISC) leading to decomposition in low-lying quintet or triplet states. Photons in three different energy ranges are considered, yellow (\(<1.5\) eV), green (\(\sim 2\) eV), blue (\(\sim 2.4\) eV) and purple (\(\sim 3.8\) eV). While no fragmentation is possible at low photon energies (yellow), increasing excitation energies (green) allow for water loss while water splitting becomes accessible with more energy (blue) in the triplet manifold. Here, hydrogen molecule elimination via a TS (blue) is possible. Hydrogen radical loss and water elimination become increasingly important with increasing photon energies (purple).
beams (Fig. S4, ESIT). The breakdown curves indicate that water activation requires collision energies well above 50 eV. Both CID experiments are consistent with the inaccessibility of the quintet-triplet crossing region in Fig. 2 from the quintet ground state.

Unfortunately, the effort involved in the calculation of the excited state potential energy surfaces shown in Fig. 2 and Fig. S5 (ESI†) grows with each additional H2O molecule. This makes a numerical evaluation extremely difficult and restricts our analysis to the smallest cluster studied. Since the excitations are taking place in the valence shell of the V center, modified by the interaction with the water ligands, the number of accessible states most likely increases significantly due to the redshift of the absorptions. In turn, reaching conical intersections and intersystem crossings should become more facile with increasing hydration, due to the increased conformational flexibility.

Nevertheless, the analysis of Fig. 3a on the quintet ground state and lowest lying triplet state potential energy surfaces can readily be extended to larger clusters. Fig. 3b shows accessible decomposition pathways leading to H2O loss, H atom loss, and H2 formation for V*(H2O)4. Again, H2O evaporation preferentially occurs on the quintet PES, with a slightly reduced binding energy of 1.51 eV. Also, direct evaporation of an H atom is possible on the quintet PES, but the transition state TS2 lies with 2.26 eV still above TS1 for the H atom transfer to the metal center. H atom loss will thus proceed by H atom migration via TS1 to the metal center, preferentially on the triplet PES, followed by a barrierless evaporation from I2. The switch from quintet to triplet will occur shortly before reaching TS1. In I2, the oxidation of V(i) to V(m) is completed in triplet, with an energetically favorable hydride-metal-hydroxide arrangement. With the second H2O molecule, the product ion remaining after H2 formation is now either the hydrated metal oxide or a metal dihydroxide. Since the pathway to the dihydroxide via TS4 faces a 0.35 eV lower barrier than the hydrated metal oxide pathway via TS3, with a similar energy difference in the product energies, H2 formation will preferentially proceed towards the metal dihydroxide product.

Table 1

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* The threshold was determined as the point where the three-point running average of a fragment surpasses twice the three-point running average of the noise level.
the probability for reaching the ground state. This explains the clear dominance of the H$_2$O loss pathway. During the radiation-less relaxation, ISC readily occurs. When the system has reached the lowest-lying triplet state, passage via TS1 to the inserted hydride-hydroxide structure [HVOH(H$_2$O)$_{n-1}$]$^+$ is energetically preferred over H$_2$O loss. Once I$_2$ is reached, H$_3$ elimination may seem inevitable, given the profound energetic preference of TS3 over the H atom loss. However, the thresholds in Table 1 indicate that H atom formation occurs with significant excess energy in the experiment, at least 1.3 eV, 0.3 eV and 0.5 eV for $n = 2, 3, 4$, respectively. This may make the high-lying loose transition state for H elimination competitive with the tight transition state for H$_2$ loss. With increasing photon energy, the branching ratio of H atom loss increases, in line with this statistical interpretation. An alternative explanation would be a specific excited state or a set of excited states with a repulsive region along the O–H dissociation coordinate, which may be present at higher excitation energies around the FC point, but we see no realistic way to investigate this idea further.

**Potential contribution of multi-photon processes.** With the pulse energies of a nanosecond OPO system without tight focusing of the laser beam, as used here, non-resonant multi-photon processes are extremely unlikely. Resonant two-photon processes, on the other hand, are in principle possible in this experimental configuration, and have been identified in previous studies for selected absorption bands. In these cases, however, the apparent single-photon cross sections were significantly smaller than in the present study. The most likely candidates for two-photon processes in the present study would be the weak 3d–3d transitions in Fig. 1. Here the broad spectral range investigated is helpful: if these absorptions were significantly influenced by two-photon processes, the photochemistry should be similar to the bands with twice the photon energy. This is, however, clearly not the case. For $n = 1$, VOH$^+$ is the dominant ionic photoproduct at high energies, but is only weakly observed below 3 eV. For $n = 2$, the weak band features exclusively water loss, while H and H$_2$ formation are intense at higher energies. Also for $n = 3$ and $n = 4$, formation of molecular and atomic hydrogen is more prominent at higher photon energies. Unless one postulates that also the high energy absorptions are two-photon processes, the branching ratio of the photoproducts is direct evidence that two-photon processes do not play a major role. However, if the absorptions on the blue end of the spectra were also two-photon processes, the available energy in the system would be > 7 eV, and much more severe fragmentation of the clusters should be expected. All things considered, the most consistent interpretation of the results is in terms of photochemistry following absorption of a single photon.

**Photodissociation of V$^+$(H$_2$O)$_{5-20}$**

Larger clusters show an intense broad feature from typically 2.0 to 3.2 eV, with additional weaker absorptions towards lower and higher energies, see Fig. 5. The strong red-shift of the most intense band previously observed up to $n = 4$ levels off when moving to $n = 5$, and no systematic shift is evident for larger clusters. This observation is in line with earlier infrared spectroscopy that the first solvation shell is fully occupied with four water molecules. Further hydration in the second solvation shell does not significantly affect the electronic structure of the V$^+$ ion in the core and mostly broadens the bands.

BIRD triggering the intracluster hydrogen elimination reaction becomes increasingly important for larger clusters. In combination with the correction for the laser pulse energy, which is proportional to the inverse pulse energy, see Fig. S3 (ESI†), identifying signal close to the noise level is getting
difficult, especially in the region of 3.0–3.5 eV, where the laser power is inherently low due to the switch from the OPO signal to the SFG stage. The signal above 3.5 eV for \( n = 8-12 \) in Fig. 5 may thus be an artifact due to insufficient BIRD correction. Nevertheless, the key features of the spectra can be assigned. The absorption cross section from \( n = 9 \) to 12 shows a decrease with increasing cluster size. This indicates that the insertion reaction from \( V^+(\text{H}_2\text{O})_{n-1} \) to \([\text{HVOH}(\text{H}_2\text{O})_{n-1}]^+\) with the oxidation of the vanadium center from \( V^0 \) to \( V^+ \) takes place. The \([\text{HVOH}(\text{H}_2\text{O})_{n-1}]^+ \) species is almost transparent in the measured spectral range, see Fig. S2 in the ESI† for a calculated spectrum of \( n = 8 \). A decrease in the photodissociation cross section indicates that the fraction of the inserted species \([\text{HVOH}(\text{H}_2\text{O})_{n-1}]^+ \) in the ion population is increasing for larger clusters. For \( n \geq 15 \), no more photoinduced fragmentation is observed, see Fig. S1 (ESI†) for sizes \( n = 20, 30 \) and 41. This means that all the clusters completed the insertion reaction, and only \([\text{HVOH}(\text{H}_2\text{O})_{n-1}]^+ \) with \( V^+ \) is present.

For \( n = 5-9 \), the H\textsubscript{2}O loss dominates in the low energy range with \( H + \text{H}_2\text{O} \) becoming increasingly important towards the higher energy range of the spectrum, while almost no \( H_2 + \text{H}_2\text{O} \) loss can be observed. This is comparable to the case of \( n = 4 \), as water just adds to the second solvation shell and does not change the electronic structure of the \( V^+ \) core. However, the trend slightly changes starting from \( n = 8 \), and water loss is the dominant decomposition path across the whole band for \( n = 9-12 \).

Based on the behavior of the branching ratio curves at the switch point between the OPO signal and SFG stages, \(< 410 \text{ nm or } > 3.04 \text{ eV}, \) significant contributions from multi-photon processes can be ruled out. Since the laser pulse energy drops dramatically at the switch point, multiphoton processes would become evident by drastic discontinuities in the photofragment curves of Fig. 5, but no such behavior is observed. However, secondary photon absorption is significant, in particular at the maximum of the absorption in the signal region of the OPO, around 2.5–3 eV. This is accounted for in the assignment of photoproducts for the branching ratio of the photodissociation products. Table S4 lists the assignment of all observed photofragments to either primary water-only loss or to primary \( H_2 \) formation. E.g. for \( n = 9 \), \([V\text{OH}(\text{H}_2\text{O})_9]^+ \) is assigned to the water loss channel, since it is formed from \( V^+(\text{H}_2\text{O})_m \) photodissociation products after absorption of a second photon.

The observed decomposition trend towards reduced \( H \) loss with increasing cluster size could be related to the transition of an almost planar structure to a 3D structure of the solvation shell, which has previously been discussed within infrared experiments starting at a cluster size of about \( n = 10 \). A 3D solvation shell structure with a different geometry might be able to access different conical intersections and change the photochemistry, but also steric reasons like an emerging cage effect may play a role in this subtle balance between the dissociation channels.

For the inserted structures, \([\text{HVOH}(\text{H}_2\text{O})_{n-1}]^+ \), up to \( n = 20 \), \( H_2 \) elimination is observed from BIRD fragmentation competing with slow water evaporation. However, in larger clusters \((n = 30, 41)\) this trend again shifts towards slow water loss.
related to the onset of $[\text{HVOH(H}_2\text{O})_{n-1}]^+$ formation. The upper size limit seems to correlate with the hindered proton transfer in larger $[\text{HVOH(H}_2\text{O})_{n-1}]^+$, most likely caused by the decreased structural flexibility of a rigid hydrogen-bonded water network around the V(III) center in clusters with more than $\approx 24$ water molecules.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This project was financed by the Austrian Science Fund (FWF) through project no. P29174 and within the DK-ALM: W1259-N27. The computational results presented have been achieved using the HPC infrastructure LEO of the University of Innsbruck. The tunable OPO system is part of the Innsbruck Laser Core Facility, financed by the Austrian Federal Ministry of Science, Research and Economy. Preliminary calculations have been performed by Ina Gernert and Simone Schirra.

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