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ARTICLE

Threshold ionization spectroscopy of H₂O, HDO and D₂O and low-lying vibrational levels of HDO⁺ and D₂O⁺Clément Lauzin^{a,b}, Ugo Jacovella^a, and Frédéric Merkt^a^a*Physical Chemistry Laboratory, ETH Zürich, 8093 Zürich, Switzerland*^b*Institute of condensed Matter and Nanoscience, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium**(Received 00 Month 200x; final version received 00 Month 200x)*

Rotationally resolved photoelectron spectra of jet-cooled H₂O, HDO and D₂O have been recorded near the origin of the $\tilde{X}^+ \leftarrow \tilde{X}$ photoionizing transition following single-photon ionization using the complementary techniques of MATI and PFI-ZEKE photoelectron spectroscopy. A gas mixture of H₂O, HDO and D₂O with Ar was obtained by mixing H₂O (ℓ) and D₂O (ℓ) in a reservoir and bubbling Ar gas through the mixture. To unambiguously assign the photoelectron bands to H₂O, HDO or D₂O, the PFI-ZEKE photoelectron spectra of the mixture were compared to MATI spectra and to spectra of H₂O. Analysis of the rotational structure of the origin bands ($v_1^+ = 0, v_2^+ = 0, v_3^+ = 0$) $\leftarrow$ ($v_1 = 0, v_2 = 0, v_3 = 0$) of H₂O, HDO and D₂O and of the transitions to the (0,1,0), (0,2,0) and (1,0,0) levels of D₂O⁺ and the first excited level of the O-D stretching mode of HDO⁺ provided new information on the photoionization dynamics of water and the energy level structure of HDO⁺ and D₂O⁺.

Keywords: PFI-ZEKE photoelectron spectroscopy; water; MATI

1. Introduction

Water (H₂O) and its cation (H₂O⁺) are prototypical small molecules [1] and play an important role on earth and in the universe. Studies of H₂O, HDO and D₂O by vacuum-ultraviolet photoelectron and photoionization spectroscopy provide information on their interaction with short-wavelength radiation, on their photoionization dynamics, and on the energy level structure and dynamics of the cations [2–16]. The valence-shell photoionization of water, either in a single-photon process from the $\tilde{X}^1A_1$ ground state or in multiphoton processes through electronically excited states, has provided access to a wide range of rovibrational levels of the $\tilde{X}^+^2B_1$ and $\tilde{A}^+^2A_1$ states of the cation, which are degenerate in linear ($D_{\infty h}$) configurations and subject to the Renner-Teller effect [17–19]. Whereas H₂O⁺ in the first excited state is quasilinear, the equilibrium geometry of the ground cationic state is bent and similar to that of the ground state of the neutral. Consequently, many more vibrational levels of the $\tilde{A}^+^2A_1$ state are accessible by photoionization from the ground state of the neutral than is the case for the $\tilde{X}^+^2B_1$ state [2, 4, 5, 12, 15, 16].

The VUV photoelectron spectrum of the $\tilde{X}^+^2B_1 \leftarrow \tilde{X}^1A_1$ photoionizing transition of water thus consists of only a few vibrational bands, i.e., a strong origin band and weak and short progressions in the bending ($0, v_2^+, 0$) and symmetric stretching ($v_1^+, 0, 0$) modes [4, 12, 15, 16]. The weakness of the bands associated with these progressions makes them difficult to study at high resolution, and most studies of the excited vibrational levels of the $\tilde{X}^+^2B_1$ ground state of H₂O⁺ by photo-

electron spectroscopy have not provided detailed information on their rotational structure. For H_2O^+ and D_2O^+ , the energy level structure has been determined from high-resolution spectroscopic measurements of (i) the $\tilde{\text{A}}^+ \text{}^2\text{A}_1 - \tilde{\text{X}}^+ \text{}^2\text{B}_1$ band system [20, 21], (ii) the submillimeter wave and infrared spectrum of the $\tilde{\text{X}}^+$ state in the gas phase [22–25] and (iii) the infrared spectrum in a neon matrix [26]. Considerable efforts have also been invested to obtain accurate potential-energy surfaces for the $\tilde{\text{X}}^+$ state by quantum-chemical methods and to adjust these surfaces to reproduce experimentally determined energy levels [18, 19].

The motivations for the photoelectron-spectroscopic study presented in this article was the realization that the adiabatic ionization energy of HDO was not precisely known and that hardly any photoelectron spectroscopic data had been reported for HDO. The photoionization of H_2O and D_2O is subject to strict selection rules related to the conservation of nuclear-spin symmetry [27]. In the case of HDO, the photoionization selection rules are less restrictive, and one of the goals of the research presented here was to study how this aspect manifests itself in the rotational structure of the photoelectron spectrum.

Because of the exchange of H and D nuclei in a water sample containing both nuclei, it is not possible to study the photoelectron spectrum of a pure HDO sample. Our approach was to measure the photoelectron spectrum of a mixture of H_2O , HDO and D_2O , as already done by Dixon and coworkers [4]. To unambiguously identify the spectral features of H_2O , HDO and D_2O , additional mass-selective measurements were performed using the technique of mass-analyzed threshold-ionization (MATI) spectroscopy [28]. We already exploited the same strategy in our studies of the photoionization and photoelectron spectra of ammonia [29, 30].

2. Experiment

The experiments were performed using a tunable vacuum-ultraviolet (VUV) laser source coupled to a pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectrometer previously described in Ref. [31].

A gas mixture containing H_2O , HDO and D_2O was formed by bubbling the carrier gas argon through a stainless-steel cylinder filled with approximately equal amounts of distilled H_2O (ℓ) and analytical D_2O (ℓ). The gas mixture was introduced into the photoelectron spectrometer with a pulsed valve producing a supersonic expansion. After passing a skimmer, the gas beam intersected the VUV laser beam at right angles on the axis of a set of six parallel extraction plates. Sequences of pulsed voltages were applied to these plates to field ionize the very high Rydberg states (principal quantum numbers $n \geq 200$) located below each ionization threshold and extract the electrons or ions toward a microchannel-plate detector.

PFI-ZEKE photoelectron spectra were recorded using a two-pulse sequence consisting of a first, discrimination pulsed field of +50 mV/cm, followed by a second, field-ionization and electron-extraction pulse of -1 V/cm and monitoring the electron signal as a function of the VUV wavenumber. This pulse sequence resulted in an experimental resolution of 0.8 cm^{-1} . MATI spectra were recorded using a discrimination field of -333 mV/cm and a field-ionization and ion-extraction pulse of +133 V/cm. Spectra of HDO and D_2O were recorded by monitoring the ion signals at the corresponding ion flight times. The resolution of the MATI spectra was about 2 cm^{-1} . The positions of the field-free ionization thresholds were obtained after correcting for the field-induced shifts using the procedure described in Ref. [32].

The pulsed tunable VUV laser radiation (wavenumber $\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 + \tilde{\nu}_2$, pulse length 2 ns, repetition rate 25 Hz) was produced by resonant four-wave mixing in a

pulsed beam of xenon using the $(5p)^6 \rightarrow (5p)^5 6p[1/2]_0$ two-photon resonance of Xe at $2\tilde{\nu}_1 = 80118.98 \text{ cm}^{-1}$ with commercial pulsed dye lasers and standard frequency-doubling methods to generate the radiation at the wavenumbers $\tilde{\nu}_1$ and $\tilde{\nu}_2$. The VUV laser bandwidth was 0.5 cm^{-1} and the VUV wavenumber was calibrated with an accuracy of 0.5 cm^{-1} by recording optogalvanic spectra of argon with the fundamental outputs of the dye lasers.

3. Results

3.1. Rovibronic photoionization selection rules

$\text{H}_2\text{O}^{(+)}$, $\text{HDO}^{(+)}$ and $\text{D}_2\text{O}^{(+)}$ are asymmetric-top molecules in the electronic ground state of the neutral molecule and of the cation. To label the rotational levels of the neutral molecule and the ion, we use the notation $N_{K_a'' K_c''}''$ and $N_{K_a^+ K_c^+}^+$, respectively, where N represents the rotational-angular-momentum quantum number and K_a and K_c the quantum numbers associated with the projection of the rotational angular momentum vector onto the a and c principal axes. The principal-axis system is depicted in Fig. 1, which also shows schematically the highest occupied molecular orbital, an orbital of b_1 symmetry and mainly p ($\ell = 1$) character centered on the O atom. In an atom, single-photon ionization out of a p orbital would be accompanied with the ejection of even- ℓ (s and d) photoelectron partial waves. Rovibronic photoionization transitions are characterized by the changes $\Delta N = N^+ - N''$, $\Delta K_a = K_a^+ - K_a''$ and $\Delta K_c = K_c^+ - K_c''$ resulting from the photoionization process. Specific transitions are labeled $N_{K_a^+ K_c^+}^+ - N_{K_a'' K_c''}''$.

The general rovibronic photoionization selection rules for molecular photoionization are [27]

$$\Gamma_{\text{rve}}^+ \otimes \Gamma_{\text{rve}}'' \supset \Gamma^* \text{ for } \ell \text{ even,} \quad (1)$$

and

$$\Gamma_{\text{rve}}^+ \otimes \Gamma_{\text{rve}}'' \supset \Gamma^{(s)} \text{ for } \ell \text{ odd,} \quad (2)$$

where $\Gamma_{\text{rve}}^{+''}$ represents the rovibronic symmetry of the ionic (+) or the neutral (") species, $\Gamma^{(s)}$ and Γ^* are the totally symmetric representation and the dipole-moment representation (i.e., the representation having the character -1 for all operations involving an inversion, and the character $+1$ otherwise) of the relevant molecular-symmetry group, respectively, and ℓ is the angular-momentum quantum number of the photoelectron partial wave. In the case of H_2O and D_2O , which belong to the $\text{C}_{2v}(\text{M})$ molecular-symmetry group, for which $\Gamma^{(s)} = A_1$ and $\Gamma^* = A_2$ [1], one obtains from Eqs. (1) and (2)

$$A_1 \longleftrightarrow A_2, B_1 \longleftrightarrow B_2 \quad (3)$$

or

$$\Delta K_a = K_a^+ - K_a'' = \text{odd}, \quad \Delta K_c = K_c^+ - K_c'' = \text{even} \quad (4)$$

for even values of ℓ , and

$$A_1 \longleftrightarrow A_1, A_2 \longleftrightarrow A_2, B_1 \longleftrightarrow B_1, B_2 \longleftrightarrow B_2, \quad (5)$$

or

$$\Delta K_a = \text{even}, \quad \Delta K_c = \text{odd} \quad (6)$$

for odd values of ℓ , as explained in Ref. [27].

In both H₂O and D₂O, the conservation of nuclear-spin symmetry in photoionization forbids transitions of the type $A_i \longleftrightarrow B_j$ ($i, j = 1, 2$) between ortho levels [i.e., rovibronic levels of B₁ or B₂ (A₁ or A₂) symmetry and a spin-statistical weight of 3 (6) in H₂O (D₂O)] and para levels [rovibronic levels of A₁ or A₂ (B₁ or B₂) symmetry and a spin-statistical weight of 1 (3) in H₂O (D₂O)]. The p character of the b_1 valence orbital out of which the electron is ejected tends to favor the emission of even- ℓ (s and d) photoelectron partial waves, a tendency we refer to as the even- ℓ propensity below. However, previous work on the photoionization of H₂O has indicated that the photoelectron can also be ejected as odd- ℓ partial waves as a result of rotational channel interactions mediated by the dipole moment of the ion core [7, 8, 11, 13, 27, 33] and the deviation of the b_1 valence orbital from a pure $\ell = 1$ orbital.

In a crude "orbital" approximation of the photoionization process [34], the ejection of an electron out of the b_1 valence orbital (see Fig. 1), which has a nodal plane containing the a axis (π symmetry for a linear configuration), can be expected to favor transitions with $\Delta K_a = \pm 1$, a tendency we refer to as the $\Delta K_a = \pm 1$ propensity below. Consequently, one can distinguish between three types of transitions in H₂O and D₂O, (i) those obeying Eqs. (3) and (4), which should be dominant, particularly when $\Delta K_a = \pm 1$, (ii) those obeying Eqs. (5) and (6), and (iii) those with either $\Delta K_a = \text{odd}$ and $\Delta K_c = \text{odd}$ or $\Delta K_a = \text{even}$ and $\Delta K_c = \text{even}$, which are strictly forbidden.

In the C_s(M) molecular-symmetry group appropriate for HDO, $\Gamma^{(s)} = A'$ and $\Gamma^* = A''$ [1], and the rovibronic photoionization selection rules can be expressed as

$$A' \longleftrightarrow A'', \quad (7)$$

or

$$\Delta K_a = \text{even or odd}, \quad \Delta K_c = \text{odd} \quad (8)$$

for even values of ℓ , and

$$A' \longleftrightarrow A', \quad A'' \longleftrightarrow A'' \quad (9)$$

or

$$\Delta K_a = \text{even or odd}, \quad \Delta K_c = \text{even} \quad (10)$$

for odd values of ℓ .

These selection rules imply that all rovibronic photoionization transitions are allowed in the $\tilde{X}^+ \ ^2B_1 \leftarrow \tilde{X} \ ^1A_1$ band system of HDO, even those for which both ΔK_a and ΔK_c are even and the photoelectron is ejected as odd- ℓ partial waves. Because of the similarity of the structure of the ionic and neutral species in their respective ground electronic state, transitions with $\Delta N = 0$, $\Delta K_a = 0$ and $\Delta K_c = 0$ should give rise to an accumulation of close-lying lines in the photoelectron spectrum of HDO, which might make them observable.

3.2. Threshold ionization spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of H₂O, D₂O and HDO

The PFI-ZEKE photoelectron spectrum of the mixture of H₂O, HDO and D₂O in the region of the origin of the $\tilde{X}^+ \ ^2B_1 \leftarrow \tilde{X} \ ^1A_1$ photoionizing transition is presented in Fig. 2b. It consists of about 30 irregularly spaced lines, the narrowest having a full width at half maximum of $\approx 0.8 \text{ cm}^{-1}$. Because the origin bands of H₂O, HDO and D₂O overlap, the attribution of the different lines to a given species was made by comparison with the PFI-ZEKE photoelectron spectrum of H₂O (from Ref. [11]) and the MATI spectra of HDO and D₂O, which are displayed in Fig. 2a. The assignment of the transitions of H₂O and D₂O was made by direct comparison with earlier PFI-ZEKE photoelectron spectra [7, 11]. Because full and accurate sets of molecular constants are available in the literature on the ground vibronic states of H₂O [35], H₂O⁺ [22], D₂O [36], and D₂O⁺ [37], we utilized them to derive the adiabatic ionization energies of H₂O (101766.3(10) cm⁻¹) and D₂O (101915.2(10) cm⁻¹) in a least-squares fit. These values are in agreement with those observed in earlier studies [7, 11] (see Table 3). In the case of HDO, we used the precisely known energy-level structure of the $\tilde{X}$ (000) state [38] to determine the adiabatic ionization energy ($E_i = 101840.1(10) \text{ cm}^{-1}$) and estimate the rotational constants ($A_0^+ = 23.5(5) \text{ cm}^{-1}$, $B_0^+ = 7.8(2) \text{ cm}^{-1}$, and $C_0^+ = 6.0(2) \text{ cm}^{-1}$) of the ground state of HDO⁺ from the experimental line positions. The large uncertainties in the rotational constants result from the small number of observed transitions and their width of about 0.8 cm^{-1} .

In all three molecules, we not only observe strong $\Delta K_a = \pm 1$ transitions, but also a smaller number of in general weaker $\Delta K_a = 0$ transitions, in accord with previous observations [7, 11, 13, 33]. A specific feature of the spectrum of HDO are weak transitions with $\Delta K_a = \Delta K_c = 0$, which are strictly forbidden in the photoelectron spectra of H₂O and D₂O. Several of these transitions, e.g. $0_{00} - 0_{00}$, $1_{10} - 1_{10}$, $1_{01} - 1_{01}$, and $1_{11} - 1_{11}$, accumulate within a narrow wavenumber range, which facilitates their observation (see regions labeled "Q" in Figs. 2 and 4). Interestingly, these transitions are significantly weaker than those with $\Delta K_a = 0$, $\Delta K_c = 1$ (see, e.g., the strong $1_{01} - 0_{00}$ transition in Figs. 2 and 4)), which indicates that the violation of the $\Delta K_a = \pm 1$ propensity is not the sole reason for their weakness. In H₂O and D₂O, $\Delta K_a = \text{even}$ rovibronic photoionization transitions are always accompanied by the emission of odd- ℓ partial waves (see Eqs. (5) and (6)). It is thus not possible to find out experimentally which of the $\Delta K_a = \pm 1$ or the ℓ -even propensity rules is the more stringent one. In HDO, both even- ℓ (with $\Delta K_c = \text{odd}$) and odd- ℓ (with $\Delta K_c = \text{even}$) partial waves are allowed by the general rovibronic photoionization selection rules for $\Delta K_a = \text{even}$ transitions. The relative intensities of the $\Delta K_a = 0$ rovibronic transitions observed in the spectrum of HDO suggests that the ℓ -even propensity rule is more stringent than the $\Delta K_a = \pm 1$ propensity rule.

All strong transitions in Fig. 2a and b originate from the lowest possible rotational levels, i.e., the 0_{00} level in the case of HDO, para H₂O and ortho D₂O and the 1_{01} level in the case of ortho H₂O and para D₂O. Consequently, no significant conversion between ortho and para levels takes place during the formation of the supersonic beam in our experiments, which indicates that H₂O (D₂O, HDO) monomer collisions with the carrier gas Ar dominate the cooling process (see discussion in Ref. [39]). Tables 1 and 2 list the positions and assignments of the dominant transitions observed in the PFI-ZEKE photoelectron spectrum of HDO and D₂O and the values of their adiabatic ionization energies.

3.3. The (010), (020) and (100) vibrational levels of D_2O^+ and the fundamental of the O-D stretching mode of HDO^+

The bands of the photoelectron spectrum of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of water associated with excited vibrational levels of the cation are weak. In the case of H_2O and D_2O , the most complete set of level positions was reported by Truong *et al.* [15] who determined all $(v_1^+, v_2^+, 0)$ ionization thresholds up to about 1 eV of internal energy in the cation (see Tables 4 and 5 of Ref. [15]). The relative positions of the cation energy levels they derived agree within about 3 meV with the positions extracted in earlier photoelectron spectroscopic studies [3, 4]. All three fundamental vibrational wave numbers of D_2O^+ and HDO^+ were also determined from the vibrational spectrum of the cations in solid neon matrices [26]. The most precise determinations of the positions of low-lying vibrational levels of D_2O^+ reported to date are those of the (100) level by photoionization spectroscopy and Rydberg extrapolation techniques [6, 40] and of the (010) level by infrared spectroscopy of the cation [37].

Next to the origin band of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition, our VUV laser also provided access to the $\tilde{X}^+$ (010), (020) and (100) $\leftarrow \tilde{X}$ (000) photoelectron bands of D_2O and of the transition to the fundamental of the O-D stretching mode of HDO^+ . Because of the weakness of these transitions, already noted in previous studies [4, 15], the spectra we obtained had a poor signal-to-noise ratio and only the strongest lines could be unambiguously observed.

The PFI-ZEKE photoelectron spectrum of the $\tilde{X}^+$ (010) $\leftarrow \tilde{X}$ (000) band of D_2O is presented in Fig. 3 and consists of the four strong lines characteristic of transitions to symmetric vibrational levels of D_2O^+ (see Fig. 2). A similar structure is observed in the PFI-ZEKE photoelectron spectrum of the mixture of H_2O , HDO and D_2O near 104000 cm^{-1} (see Fig. 4), and is assigned to the $\tilde{X}^+$ (020) $\leftarrow \tilde{X}$ (000) band of D_2O . The spectrum depicted in Fig. 4 also contains a stronger band near 104250 cm^{-1} . In this region, the $\tilde{X}^+$ (100) $\leftarrow \tilde{X}$ (000) band of D_2O overlaps with the transition to the (0,1,0) level of HDO^+ (fundamental of the OD-stretching mode; in the ground electronic states of HDO and HDO^+ , all three vibrational modes are totally symmetric, so that this mode is labeled ν_2 according to the usual convention consisting of ordering modes by symmetry and decreasing wavenumbers). Because the bands presented in Figs. 3 and 4 all involve transitions to totally symmetric vibrational levels, the same rovibronic selection rules apply as for the origin bands, which made the analysis of the rotational structure straightforward. To determine the positions of the (010) and (020) vibrational levels of D_2O^+ , we used the rotational constants of the (000) and (010) levels of D_2O^+ reported by Duan *et al.* [37], which we extrapolated linearly to obtain estimates of the rotational constants of the (020) level, and adjusted the ionization energies in a least-squares fit. For the (100) level of D_2O^+ and the (010) level of HDO^+ we used, in first approximation, the rotational constants obtained from the analysis of the origin band. The $\tilde{X}^+$ (010) $\leftarrow \tilde{X}$ (000) band of HDO shows the characteristic broader feature associated with close-lying $\Delta N = \Delta K_a = \Delta K_c = 0$ "Q-type" transitions already discussed in the previous subsection. The main transitions observed in the spectra of HDO and D_2O are summarized in Tables 1 and 2 with the molecular constants used to derive the ionization energies.

Table 3 summarizes the ionization energies of H_2O , HDO and D_2O and the vibrational level positions of the corresponding cations determined from our spectra and compares them with the results of earlier studies. The position of the (010) band of D_2O^+ is in agreement with, but less precise than, the value obtained by Duan *et al.* [37]. The position of the (100) band of D_2O^+ agrees with the earlier results of Page *et al.* [6] and Child and Jungen [40], but is slightly more precise. The

positions of the (020) and (100) levels of D₂O⁺ and the (010) (OD stretch) level of HDO⁺ are determined here for the first time from rotationally resolved spectra. Taking into account the shifts expected from the interaction of the ions with the neon matrix, our results are compatible with those obtained from the IR spectra of HDO⁺ and D₂O⁺ in solid neon [26]. A small deviation of $\approx 3.5 \text{ cm}^{-1}$ between the positions of the bending levels (010) and (020) of D₂O⁺ determined here and those calculated from the adjusted *ab initio* potential energy surface [18, 19] demonstrates the good quality of this surface.

4. Conclusions

High-resolution photoelectron spectra of a gas-phase mixture of H₂O, HDO and D₂O near the origin of the $\tilde{X}^+ \ ^2B_1 \leftarrow \tilde{X} \ ^1A_1$ photoionizing transition have provided information on the photoionization of water, on the adiabatic ionization energy of HDO (101840.1(10) cm^{-1}), the fundamental wavenumber of the O-D stretching mode of HDO⁺ (2385.4(10) cm^{-1}), and the overtone of the bending mode of (2066.4(10) cm^{-1}) and the fundamental of the symmetric stretching mode (2347.9(20) cm^{-1}) of D₂O⁺. The positions of several low-lying vibrational levels of D₂O⁺ and HDO⁺ were compared with earlier experimental and theoretical results, with which they are in good agreement. A discrepancy of only $\approx 3.5 \text{ cm}^{-1}$ between the positions of the first two excited bending levels of D₂O⁺ determined here and those obtained from the adjusted *ab initio* potential energy surface reported in Refs. [18, 19] demonstrates the quality of this surface near the equilibrium structure and provides a basis for a future refinement. In the photoelectron spectrum of HDO, rovibronic photoionization transitions with $\Delta K_a = \Delta K_c = 0$ were observed, which require the emission of odd- ℓ photoelectron partial waves and do not follow the $\Delta K_a = \pm 1$ propensity rule expected for ionization out of an orbital with a nodal plane coinciding with the molecular plane. The comparison of their intensities with those of ($\Delta K_a = 0$, $\Delta K_c = 1$) transitions, which also violate the $\Delta K_a = \pm 1$ propensity rule but require the emission of even- ℓ photoelectron partial waves, indicates that the propensity for the emission of even- ℓ partial wave is stronger than the $\Delta K_a = \pm 1$ propensity.

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Tables

	(0,0,0)	(0,1,0)	$N_{K_a^+K_c^+}^+$	$N_{K_a''K_c''}''$
1	101808.6		0 ₀₀	1 ₁₀
2	101821.1		1 ₀₁	1 ₁₀
3 ^a	101824.5	104209.7	1 ₀₁	1 ₁₁
4	101837.8		1 ₁₁	1 ₁₀
5	101840.2	104224.6	"Q"	
6 ^b	101853.7	104238.9	1 ₀₁	0 ₀₀
7	101865.9		2 ₀₂	1 ₀₁
8	101871.4	104256.9	1 ₁₀	0 ₀₀
9	101885.4	104271.2	2 ₁₁	1 ₀₁
A^+	23.5 (5)			
B^+	7.8 (2)			
C^+	6.0(2)			
$E_I/(hc)$	101840.1 (10)	104225.5(20)		
$E_{vib}/(hc)$		2385.4(10)		

Table 1. Assignments and positions of the lines observed in the PFI-ZEKE photoelectron and MATI spectra of HDO. The ionization energies corresponding to the (000) and (010) levels of the ground electronic state of the HDO^+ cation are also indicated with the rotational constants used to derive them. The positions of the ionization thresholds have been corrected by adding the field-induced shifts caused by the different field-ionization pulse sequences. All values are in cm^{-1} .

^a Line overlaps with 0₀₀ – 1₀₁.

^b Line overlaps with 1₁₁ – 1₀₁.

	(0,0,0)	(0,1,0)	(0,2,0)	(1,0,0) ^a	$N_{K_a^+K_c^+}^+$	$N_{K_a''K_c''}''$
1	101903.2	102948.3	103968.5	-	0 ₀₀	1 ₀₁
2	101905.8	102951.1	103972	-	1 ₀₁	1 ₁₁
3	101923.5			104271.4	1 ₁₁	1 ₀₁
4	101926.0	102969.9	103993.5	104273.8	1 ₀₁	0 ₀₀
5	101937.4	102984.0	104007	104285.2	1 ₁₀	0 ₀₀
6	101948.0	-	104018	104296.5	2 ₁₁	1 ₀₁
A^+	16.0562 ^b	17.697 ^b	19.338 ^c			
B^+	6.235 ^b	6.261 ^b	6.287 ^c			
C^+	4.408 ^b	4.350 ^b	4.292 ^c			
$E_I/(hc)$	101915.2(10)	102960.0(20)	103981.6(20)	104263.1(30)		
$E_{vib}/(hc)$	0	1044.8(10)	2066.4(10)	2347.9(20)		

Table 2. Assignments and positions of the lines observed in the PFI-ZEKE photoelectron and MATI spectra of D_2O . The ionization energies corresponding to the different vibrational levels of the ground electronic state of D_2O^+ are also indicated with the rotational constants used to derive them. The positions of the ionization thresholds have been corrected by adding the field-induced shifts caused by the different field-ionization pulse sequences. All values are in cm^{-1} .

^a The rotational constants of the (0,0,0) level was used in the fit of the ionization energy.

^b Rotational constants from Ref. [37] and kept fixed in the fit of the ionization energy.

^c Rotational constants linearly extrapolated from the rotational constants of the (0,0,0) and the (0,1,0) bands and kept fixed in the fit of the ionization energy.

H ₂ O (000)	HDO (000) (010)	D ₂ O (000) (010) (020) (100)	Reference
101766.3(10) 101766(2) 101772(2) 101777(7) 101795 101766.8(12)	101840.1(10)	101915.2(10) 101916(2) 101920(5) 101947(7) 101956	This work [7] [40] [6] [15] [11]
	2385.4(10) 2387.9 2365.6	1044.8(10) 1047.4 1072 1040.5 1044.28594(39)	2066.4(10) 2070.1 2089
			2347.9(20) 2350.7 2371 2392.7 2342(5) 2342(9)
			This work [19] [15] [26] [37] [40] [6]

Table 3. Adiabatic ionization energies ($E_i/(hc)$) of H₂O, HDO and D₂O and positions of the low-lying vibrational levels of HDO⁺ and D₂O⁺ determined by PFI-ZEKE photoelectron spectroscopy and comparison with earlier results. All values are in cm⁻¹.

Figure 1. Schematic representation of water (H₂O) and its principal axis system. The p-type orbital of the oxygen atom oriented parallel to the *c* axis and out of which the photoelectron is ejected in the $\tilde{X}^+ {}^2B_1 \leftarrow \tilde{X} {}^1A_1$ ionizing transition is indicated in red.

Figures

Figure 2. a) Rotationally resolved threshold ionization spectra of the origin band of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of H₂O (PFI-ZEKE photoelectron spectrum adapted from Ref. [11]), D₂O (MATI-spectrum, this work) and HDO (MATI-spectrum, this work). b) PFI-ZEKE photoelectron spectrum of a mixture of H₂O, D₂O and HDO. c) Threshold ionization spectrum calculated assuming that only $\Delta N = (0 \text{ or } 1)$, $\Delta K_a = \pm 1$ transitions carry intensity. The transitions are labeled using the notation $N_{K_a^+ K_c^+}^+ - N_{K_a'' K_c''}''$.

Figure 3. PFI-ZEKE photoelectron spectrum of the $\tilde{X}^+(010) \leftarrow \tilde{X}(000)$ transition of D_2O . The transitions are labeled using the notation $N_{K_a^+ K_c^+}^+ - N_{K_a'' K_c''}''$.

Figure 4. PFI-ZEKE photoelectron spectrum of a mixture of H₂O, D₂O and HDO in the vicinity of the $\tilde{X}^+(100)$ and $(020) \leftarrow \tilde{X}(000)$ transitions of D₂O. The spectrum also contains the transition to the fundamental level of O-D stretching mode $(0,1,0)$ of HDO⁺. The transitions are labeled using the notation $N^+_{K_a^+K_c^+} - N''_{K_a''K_c''}$.